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*Thou, nature, art my goddess; to thy laws  
My services are bound . . .  
- Carl Friedrich Gauss*

# 3

## **DIELECTRIC LOSS AND RELAXATION-I**

**T**he dielectric constant and loss are important properties of interest to electrical engineers because these two parameters, among others, decide the suitability of a material for a given application. The relationship between the dielectric constant and the polarizability under dc fields have been discussed in sufficient detail in the previous chapter. In this chapter we examine the behavior of a polar material in an alternating field, and the discussion begins with the definition of complex permittivity and dielectric loss which are of particular importance in polar materials.

Dielectric relaxation is studied to reduce energy losses in materials used in practically important areas of insulation and mechanical strength. An analysis of build up of polarization leads to the important Debye equations. The Debye relaxation phenomenon is compared with other relaxation functions due to Cole-Cole, Davidson-Cole and Havriliak-Negami relaxation theories. The behavior of a dielectric in alternating fields is examined by the approach of equivalent circuits which visualizes the lossy dielectric as equivalent to an ideal dielectric in series or in parallel with a resistance. Finally the behavior of a non-polar dielectric exhibiting electronic polarizability only is considered at optical frequencies for the case of no damping and then the theory improved by considering the damping of electron motion by the medium. Chapters 3 and 4 treat the topics in a continuing approach, the division being arbitrary for the purpose of limiting the number of equations and figures in each chapter.

### **3.1 COMPLEX PERMITTIVITY**

Consider a capacitor that consists of two plane parallel electrodes in a vacuum having an applied alternating voltage represented by the equation

$$v = V_m \cos \omega t \quad (3.1)$$

where  $v$  is the instantaneous voltage,  $V_m$  the maximum value of  $v$  and  $\omega = 2\pi f$  is the angular frequency in radian per second. The current through the capacitor,  $i_1$  is given by

$$i_1 = I_m \left( \cos \omega t + \frac{\pi}{2} \right) \quad (3.2)$$

where

$$I_m = \frac{V_m}{Z} = \omega C_0 V_m \quad (3.3)$$

In this equation  $C_0$  is the vacuum capacitance, some times referred to as geometric capacitance.

In an ideal dielectric the current leads the voltage by  $90^\circ$  and there is no component of the current in phase with the voltage. If a material of dielectric constant  $\epsilon$  is now placed between the plates the capacitance increases to  $C_0\epsilon$  and the current is given by

$$i_2 = I_m \cos \left[ \omega t + \left( \frac{\pi}{2} - \delta \right) \right] \quad (3.4)$$

where

$$I_m = \omega C_0 \epsilon V_m \quad (3.5)$$

It is noted that the usual symbol for the dielectric constant is  $\epsilon_r$ , but we omit the subscript for the sake of clarity, noting that  $\epsilon$  is dimensionless. The current phasor will not now be in phase with the voltage but by an angle  $(90^\circ - \delta)$  where  $\delta$  is called the **loss angle**. The dielectric constant is a complex quantity represented by

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (3.6)$$

The current can be resolved into two components; the component in phase with the applied voltage is  $I_x = v\omega\epsilon''C_0$  and the component leading the applied voltage by  $90^\circ$  is  $I_y = v\omega\epsilon'C_0$  (fig. 3.1). This component is the charging current of the ideal capacitor.

The component in phase with the applied voltage gives rise to dielectric loss.  $\delta$  is the loss angle and is given by

$$\delta = \tan^{-1} \frac{\epsilon''}{\epsilon'} \quad (3.7)$$

$\epsilon''$  is usually referred to as the loss factor and  $\tan \delta$  the dissipation factor. To complete the definitions we note that

$$I_x = v \omega C_0 \epsilon'' = \frac{v \omega \epsilon_0 \epsilon'' A}{d} = A \omega \epsilon_0 \epsilon'' E$$

The current density is given by

$$J_x = \frac{I_x}{A} = \omega \epsilon_0 \epsilon'' E$$

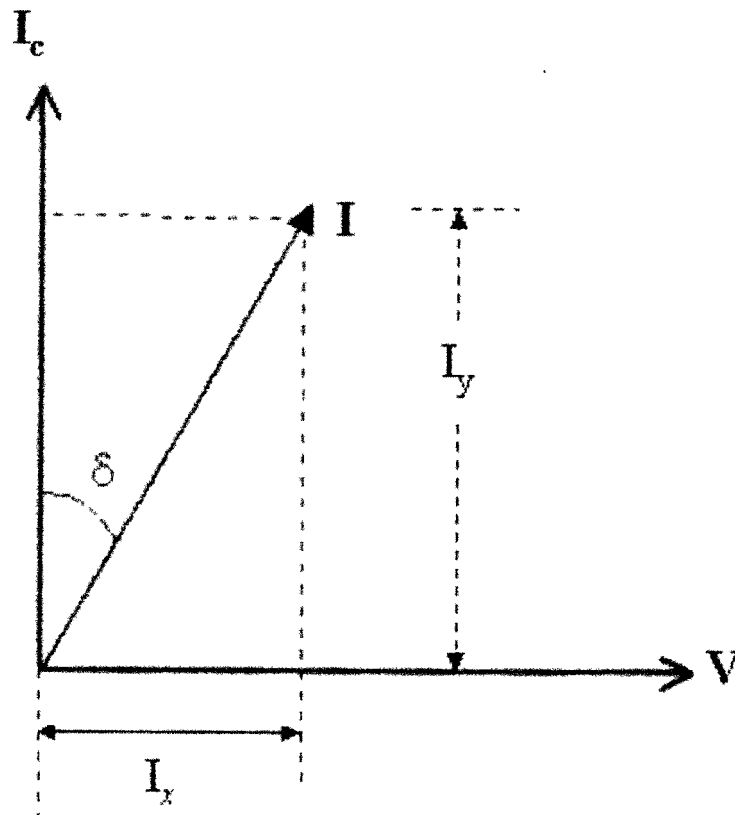


Fig. 3.1 Real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the complex dielectric constant ( $\epsilon^*$ ) in an alternating electric field. The reference phasor is along  $I_c$  and  $\epsilon^* = \epsilon' - j\epsilon''$ . The angle  $\delta$  is shown enlarged for clarity.

The alternating current conductivity is given by

$$\sigma_{ac} = \sigma' + j\sigma'' = \omega\epsilon_0 [\epsilon'' + j(\epsilon' - \epsilon_\infty)] \quad (3.8)$$

The total conductivity is given by

$$\sigma_T = \sigma_{ac} + \sigma_{dc} = \omega\epsilon_0\epsilon'' + \sigma_{dc}$$

### **3.2 POLARIZATION BUILD UP**

When a direct voltage applied to a dielectric for a sufficiently long duration is suddenly removed the decay of polarization to zero value is not instantaneous but takes a finite time. This is the time required for the dipoles to revert to a random distribution, in equilibrium with the temperature of the medium, from a field oriented alignment. Similarly the build up of polarization following the sudden application of a direct voltage takes a finite time interval before the polarization attains its maximum value. This phenomenon is described by the general term **dielectric relaxation**.

When a dc voltage is applied to a polar dielectric let us assume that the polarization builds up from zero to a final value (fig. 3.2) according to an exponential law

$$P(t) = P_\infty (1 - e^{-\frac{t}{\tau}}) \quad (3.9)$$

Where  $P(t)$  is the polarization at time  $t$  and  $\tau$  is called the relaxation time.  $\tau$  is a function of temperature and it is independent of the time.

The rate of build up of polarization may be obtained, by differentiating equation (3.9) as

$$\frac{dP(t)}{dt} = -P_\infty \left(-\frac{1}{\tau}\right) e^{-\frac{t}{\tau}} = \frac{P_\infty e^{-\frac{t}{\tau}}}{\tau} \quad (3.10)$$

Substituting equation (3.9) in (3.10) and assuming that the total polarization is due to the dipoles, we get<sup>1</sup>

$$\frac{dP(t)}{dt} = \frac{P_{\infty} - P(t)}{\tau} \cong \frac{P_{\mu} - P(t)}{\tau} \quad (3.11)$$

Neglecting atomic polarization the total polarization  $P_T(t)$  can be expressed as the sum of the orientational polarization at that instant,  $P_{\mu}(t)$ , and electronic polarization,  $P_e$  which is assumed to attain its final value instantaneously because the time required for it to attain saturation value is in the optical frequency range. Further, we assume that the instantaneous polarization of the material in an alternating voltage is equal to that under dc voltage that has the same magnitude as the peak of the alternating voltage at that instant.

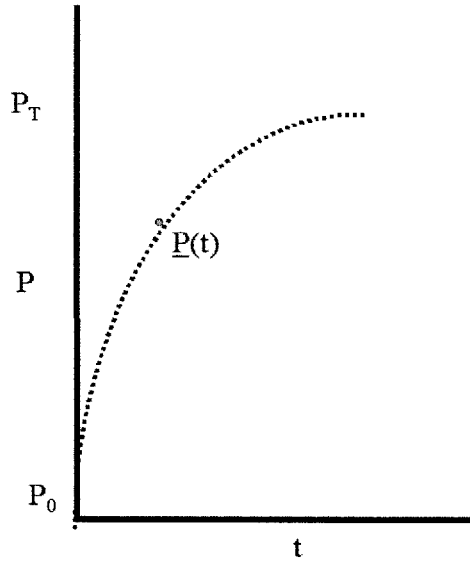


Fig. 3.2 Polarization build up in a polar dielectric.

We can express the total polarization,  $P_T(t)$ , as

$$P_T(t) = P_{\mu}(t) + P_e \quad (3.12)$$

The final value attained by the total polarization is

$$P_T = \epsilon_0(\epsilon_s - 1)E \quad (3.13)$$

We have already shown in the previous chapter that the following relationships hold under steady voltages:

$$P_e = \varepsilon_0(\varepsilon_\infty - 1)E \quad (3.14)$$

where  $\varepsilon_s$  and  $\varepsilon_\infty$  are the dielectric constants under direct voltage and at infinity frequency respectively.

We further note that Maxwell's relation

$$\varepsilon_\infty = n^2 \quad (3.15)$$

holds true at optical frequencies. Substituting equations (3.13) and (3.14) in (3.12) we get

$$P_\mu = \varepsilon_0(\varepsilon_s - 1)E - \varepsilon_0(\varepsilon_\infty - 1)E \quad (3.16)$$

which simplifies to

$$P_\mu = \varepsilon_0(\varepsilon_s - \varepsilon_\infty)E \quad (3.17)$$

Representing the alternating electric field as

$$E = E_{\max} e^{j\omega t} \quad (3.18)$$

and substituting equation (3.18) in (3.11) we get

$$\frac{dP(t)}{dt} = \frac{1}{\tau} [\varepsilon_0(\varepsilon_s - \varepsilon_\infty)E_m e^{j\omega t} - P(t)] \quad (3.19)$$

The general solution of the first order differential equation is

$$P(t) = Ce^{-\frac{t}{\tau}} + \varepsilon_0 \frac{(\varepsilon_s - \varepsilon_\infty)E_m e^{j\omega t}}{1 + j\omega\tau} \quad (3.20)$$

where C is a constant. At time t, sufficiently large when compared with  $\tau$ , the first term on the right side of equation (3.20) becomes so small that it can be neglected and we get the solution for  $P(t)$  as

$$P(t) = \varepsilon_0 \frac{(\varepsilon_s - \varepsilon_\infty) E_m e^{j\omega t}}{1 + j\omega\tau} \quad (3.21)$$

Substituting equation (3.21) in (3.12) we get

$$P(t) = \varepsilon_0(\varepsilon_\infty - 1) E_m e^{j\omega t} + \frac{\varepsilon_0(\varepsilon_s - \varepsilon_\infty)}{1 + j\omega\tau} E_m e^{j\omega t} \quad (3.22)$$

Simplification yields

$$P(t) = [\varepsilon_\infty - 1 + \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + j\omega\tau}] \varepsilon_0 E_m e^{j\omega t} \quad (3.23)$$

Equation (3.23) shows that  $P(t)$  is a sinusoidal function with the same frequency as the applied voltage. The instantaneous value of flux density  $\mathbf{D}$  is given by

$$D(t) = \varepsilon_0 \varepsilon^* E_m e^{j\omega t} \quad (3.24)$$

But the flux density is also equal to

$$D(t) = \varepsilon_0 E_m e^{j\omega t} + P(t) \quad (3.25)$$

Equating expressions (3.24) and (3.25) we get

$$\varepsilon_0 \varepsilon^* E_m e^{j\omega\tau} = \varepsilon_0 E_m e^{j\omega t} + P(t) \quad (3.26)$$

substituting equation (3.23) in (3.26), and simplifying we get

$$(\varepsilon' - j\varepsilon'') = 1 + [\varepsilon_\infty - 1 + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau}] \quad (3.27)$$

Equating the real and imaginary parts we readily obtain

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \quad (3.28)$$



$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \quad (3.29)$$

It is easy to show that

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{\varepsilon_s + \varepsilon_\infty\omega^2\tau^2} \quad (3.30)$$

Equations (3.28) and (3.29) are known as Debye equations<sup>2</sup> and they describe the behavior of polar dielectrics at various frequencies. The temperature enters the discussion by way of the parameter  $\tau$  as will be described in the following section. The plot of  $\varepsilon'' - \omega$  is known as the relaxation curve and it is characterized by a peak at  $\varepsilon''/\varepsilon''_{\max} = 0.5$ . It is easy to show  $\omega\tau = 3.46$  for this ratio and one can use this as a guide to determine whether Debye relaxation is a possible mechanism. The spectrum of the Debye relaxation curve is very broad as far as the whole gamut of physical phenomena are concerned,<sup>3</sup> though among the various relaxation formulas Debye relaxation is the narrowest. The descriptions that follow in several sections will bring out this aspect clearly.

### **3.3 DEBYE EQUATIONS**

An alternative and more concise way of expressing Debye equations is

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \quad (3.31)$$

Equations (3.28)-(3.30) are shown in fig. 3.3. An examination of these equations shows the following characteristics:

- (1) For small values of  $\omega\tau$ , the real part  $\varepsilon' \approx \varepsilon_s$  because of the squared term in the denominator of equation (3.28) and  $\varepsilon''$  is also small for the same reason. Of course, at  $\omega\tau = 0$ , we get  $\varepsilon'' = 0$  as expected because this is dc voltage.
- (2) For very large values of  $\omega\tau$ ,  $\varepsilon' = \varepsilon_\infty$  and  $\varepsilon''$  is small.
- (3) For intermediate values of frequencies  $\varepsilon''$  is a maximum at some particular value of  $\omega\tau$ .

The maximum value of  $\varepsilon''$  is obtained at a frequency given by

$$\frac{\partial \epsilon''}{\partial(\omega\tau)} = (\epsilon_s - \epsilon_\infty) \frac{(\omega^2\tau^2 - 1)}{(1 + \omega^2\tau^2)^2} = 0$$

resulting in

$$\omega_p \tau = 1 \quad (3.32)$$

where  $\omega_p$  is the frequency at  $\epsilon''_{\max}$ .

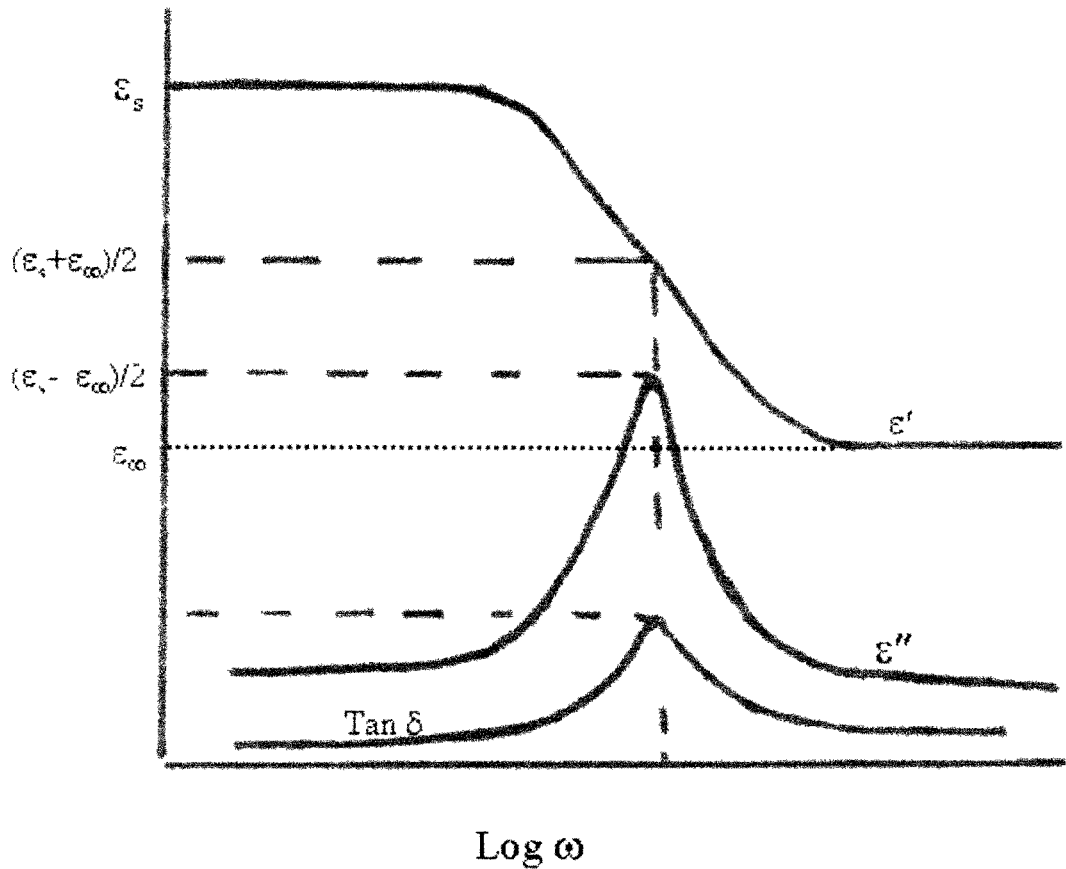


Fig. 3.3 Schematic representation of Debye equations plotted as a function of  $\log \omega$ . The peak of  $\epsilon''$  occurs at  $\omega\tau = 1$ . The peak of  $\tan \delta$  does not occur at the same frequency as the peak of  $\epsilon''$ .

The values of  $\epsilon'$  and  $\epsilon''$  at this value of  $\omega\tau$  are

$$\varepsilon' = \frac{\varepsilon_s + \varepsilon_\infty}{2} \quad (3.33)$$

$$\varepsilon''_{\max} = \frac{\varepsilon_s - \varepsilon_\infty}{2} \quad (3.34)$$

The dissipation factor  $\tan \delta$  also increases with frequency, reaches a maximum, and for further increase in frequency, it decreases. The frequency at which the loss angle is a maximum can also be found by differentiating  $\tan \delta$  with respect to  $\omega$  and equating the differential to zero. This leads to

$$\frac{\partial(\tan \delta)}{\partial(\omega\tau)} = (\varepsilon_s - \varepsilon_\infty) \frac{(\varepsilon_\infty \omega^2 \tau^2 - \varepsilon_s)}{(\varepsilon_s + \varepsilon_\infty \omega^2 \tau^2)} = 0 \quad (3.35)$$

Solving this equation it is easy to show that

$$\omega\tau = \sqrt{\frac{\varepsilon_s}{\varepsilon_\infty}} \quad (3.36)$$

By substituting this value of  $\omega\tau$  in equation (3.30) we obtain

$$(\tan \delta)_{\max} = \frac{\varepsilon_s - \varepsilon_\infty}{\sqrt{\varepsilon_s \varepsilon_\infty}} \quad (3.37)$$

The corresponding values of  $\varepsilon'$  and  $\varepsilon''$  are

$$\varepsilon' = \frac{2\varepsilon_s \varepsilon_\infty}{\varepsilon_s + \varepsilon_\infty} \quad (3.38)$$

$$\varepsilon'' = \frac{\varepsilon_s - \varepsilon_\infty}{\varepsilon_s + \varepsilon_\infty} \sqrt{\varepsilon_s \varepsilon_\infty} \quad (3.39)$$

Fig. 3.3 also shows the plot of equation (3.30), that is, the variation of  $\tan \delta$  as a function of frequency for several values of  $\tau$ .

Dividing equation (3.28) from (3.27) and rearranging terms we obtain the simple relationship

$$\frac{\epsilon''}{\epsilon' - \epsilon_{\infty}} = \omega\tau \quad (3.40)$$

According to equation (3.40) a plot of  $\frac{\epsilon''}{\epsilon' - \epsilon_{\infty}}$  against  $\omega$  results in a straight line passing through the origin with a slope of  $\tau$ .

Fig. 3.3 shows that, at the relaxation frequency defined by equation (3.32)  $\epsilon'$  decreases sharply over a relatively small band width. This fact may be used to determine whether relaxation occurs in a material at a specified frequency. If we measure  $\epsilon'$  as a function of temperature at constant frequency it will decrease rapidly with temperature at relaxation frequency. Normally in the absence of relaxation  $\epsilon'$  should increase with decreasing temperature according to equation (2.51).

Variation of  $\epsilon'$  as a function of frequency is referred to as dispersion in the literature on dielectrics. Variation of  $\epsilon''$  as a function of frequency is called absorption though the two terms are often used interchangeably, possibly because dispersion and absorption are associated phenomena. Fig. 3.4 shows a series of measured  $\epsilon'$  and  $\epsilon''$  in mixtures of water and methanol<sup>4</sup>. The question of determining whether the measured data obey Debye equation (3.31) will be considered later in this chapter.

### **3.4 BI-STABLE MODEL OF A DIPOLE**

In the molecular model of a dipole a particle of charge  $e$  may occupy one of two sites, 1 or 2, that are situated apart by a distance  $b$ <sup>5</sup>. These sites correspond to the lowest potential energy as shown in fig. 3.5. In the absence of an electric field the two sites are of equal energy with no difference between them and the particle may occupy any one of them. Between the two sites, therefore, there is a particle. An applied electric field causes a difference in the potential energy of the sites. The figure shows the conditions with no electric field with full lines and the shift in the potential energy due to the electric field by the dotted line.

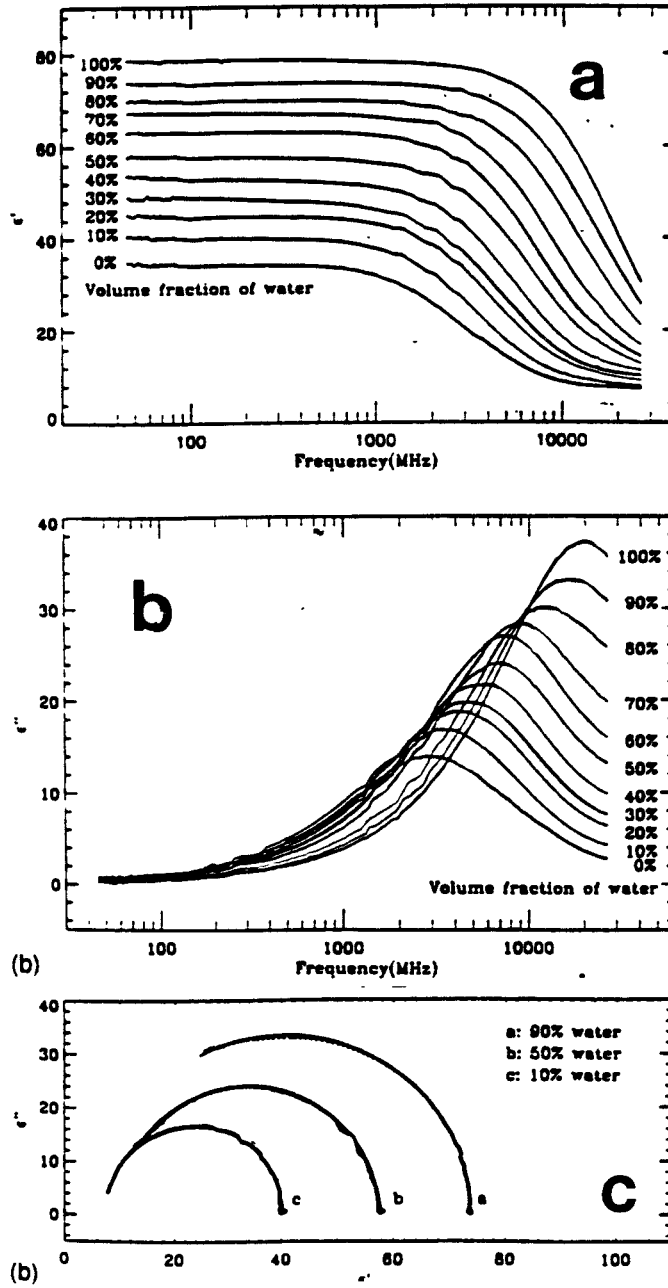


Fig. 3.4 Dielectric properties of water and methanol mixtures at 25°C. (a) Real part,  $\epsilon'$  (b) Imaginary part,  $\epsilon''$  (c) Complex plane plot of  $\epsilon^*$  showing Debye relaxation (Bao et. al., 1996). (with permission of American Physical Society.)

The difference in the potential energy due to the electric field  $E$  is

$$\phi_1 - \phi_2 = ebE \cos \theta$$

where  $\theta$  is the angle between the direction of the electric field and the line joining 1 and 2. This model is equivalent to a dipole changing position by  $180^\circ$  when the charge moves from site 1 to 2 or from site 2 to 1. The moment of such a dipole is

$$\mu = \frac{1}{2}eb$$

which may be thought of as having been hinged at the midpoint between sites 1 and 2. This model is referred to as the bistable model of the dipole. We also assume that  $\theta = 0$  for all dipoles and that the potential energy of sites 1 and 2 are equal in the absence of an external electric field.

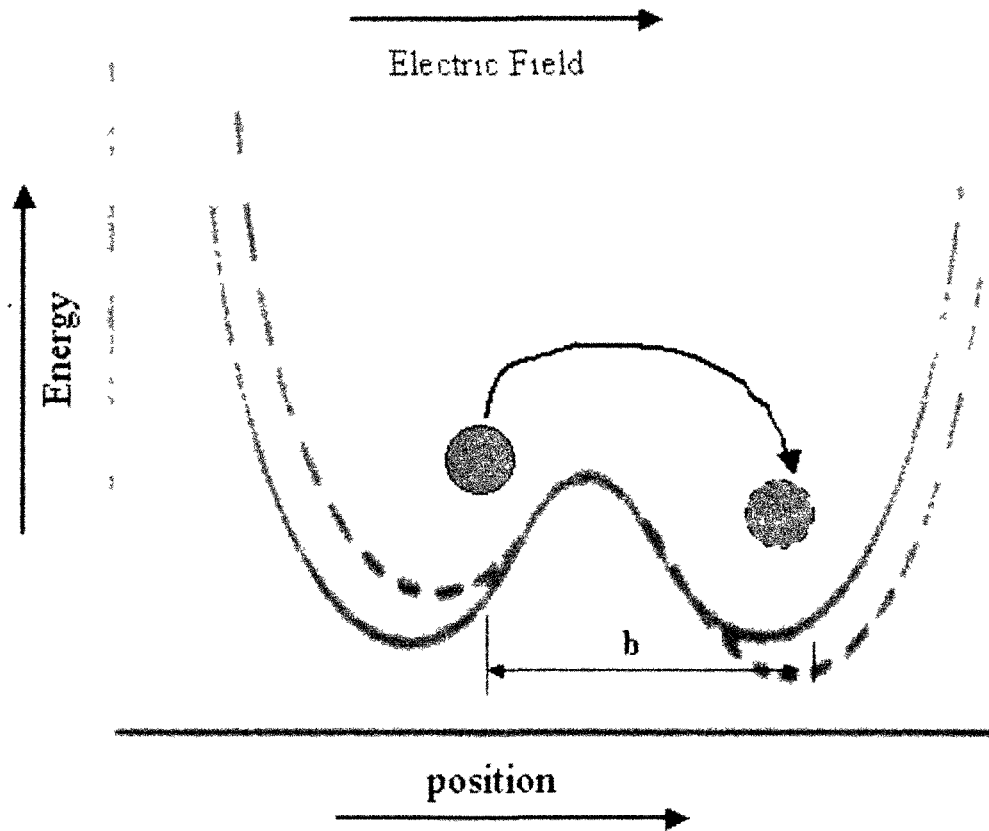


Fig. 3.5 The potential well model for a dipole with two stable positions. In the absence of an electric field (full lines) the dipole spends equal time in each well; this indicates that there is no polarization. In the presence of an electric field (broken lines) the wells are tilted with the 'downside' of the field having a slightly lower energy than the 'up' side; this represents polarization.

We assume that the material contains  $N$  number of bistable dipoles per unit volume and the field due to interaction is negligible. A macroscopic consideration shows that the charged particles would not have the energy to jump from one site to the other. However, on a microscopic scale the dipoles are in a heat reservoir exchanging energy with each other and dipoles. A charge in well 1 occasionally acquires enough energy to climb the hill and moves to well 2. Upon arrival it returns energy to the reservoir and remain there for some time. It will then acquire energy to jump to well 1 again.

The number of jumps per second from one well to the other is given in terms of the potential energy difference between the two wells as

$$W_{12} = A \exp \left[ -\frac{w - \mu E}{kT} \right]$$

where  $T$  is the absolute temperature,  $k$  the Boltzmann constant and  $A$  is a factor denoting the number of attempts. Its value is typically of the order of  $10^{13} \text{ s}^{-1}$  at room temperature though values differing by three or four orders of magnitude are not uncommon. It may or may not depend on the temperature. If it does, it is expressed as  $B/T$  as found in some polymers. If the destination well has a lower energy than the starting well then the minus sign in the exponent is valid. The relaxation time is the reciprocal of  $W_{12}$  leading to

$$\tau = \tau_0 \exp \left[ \frac{w}{kT} \right] \quad \text{for } w \gg \mu E$$

The variation of  $\tau$  with  $T$  in liquids and in polymers near the glass transition temperature is assumed to be according to this equation. Other functions of  $T$  have also been proposed which we shall consider in chapter 5. The decrease of relaxation time with increasing temperature is attributed to the fact that the frequency of jump increases with increasing temperature.

### **3.5 COMPLEX PLANE DIAGRAM**

Cole and Cole<sup>6</sup> showed that, in a material exhibiting Debye relaxation a plot of  $\epsilon''$  against  $\epsilon'$ , each point corresponding to a particular frequency yields a semi-circle. This can easily be demonstrated by rearranging equations (3.28) and (3.29) to give

$$(\epsilon'')^2 + (\epsilon' - \epsilon_\infty)^2 = \frac{(\epsilon_s - \epsilon_\infty)^2}{1 + \omega^2 \tau^2} \quad (3.41)$$

The right side of equation (3.41) may be simplified using equation (3.28) resulting in

$$(\varepsilon'')^2 + (\varepsilon' - \varepsilon_\infty)^2 = (\varepsilon_s - \varepsilon_\infty)(\varepsilon' - \varepsilon_\infty) \quad (3.42)$$

Further simplification yields

$$\varepsilon'^2 - \varepsilon'(\varepsilon_s + \varepsilon_\infty) + \varepsilon_s \varepsilon_\infty + \varepsilon''^2 = 0 \quad (3.43)$$

Substituting the algebraic identity

$$\varepsilon_s \varepsilon_\infty = \frac{1}{4}[(\varepsilon_s + \varepsilon_\infty)^2 - (\varepsilon_s - \varepsilon_\infty)^2]$$

equation (3.43) may be rewritten as

$$(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2})^2 + (\varepsilon'')^2 = (\frac{\varepsilon_s - \varepsilon_\infty}{2})^2 \quad (3.44)$$

This is the equation of a circle with radius  $\frac{\varepsilon_s - \varepsilon_\infty}{2}$  having its center at  $(\frac{\varepsilon_s + \varepsilon_\infty}{2}, 0)$ .

It can easily be shown that  $(\varepsilon_\infty, 0)$  and  $(\varepsilon_s, 0)$  are points on the circle. To put it another way, the circle intersects the horizontal axis ( $\varepsilon'$ ) at  $\varepsilon_\infty$  and  $\varepsilon_s$  as shown in fig. 3.6. Such plots of  $\varepsilon''$  versus  $\varepsilon'$  are known as complex plane plots of  $\varepsilon^*$ .

At  $\omega_p \tau = 1$  the imaginary component  $\varepsilon''$  has a maximum value of

$$\varepsilon'' = \frac{\varepsilon_s - \varepsilon_\infty}{2}$$

The corresponding value of  $\varepsilon'$  is

$$\varepsilon' = \frac{\varepsilon_s + \varepsilon_\infty}{2}$$

Of course these results are expected because the starting point for equation (3.44) is the original Debye equations.



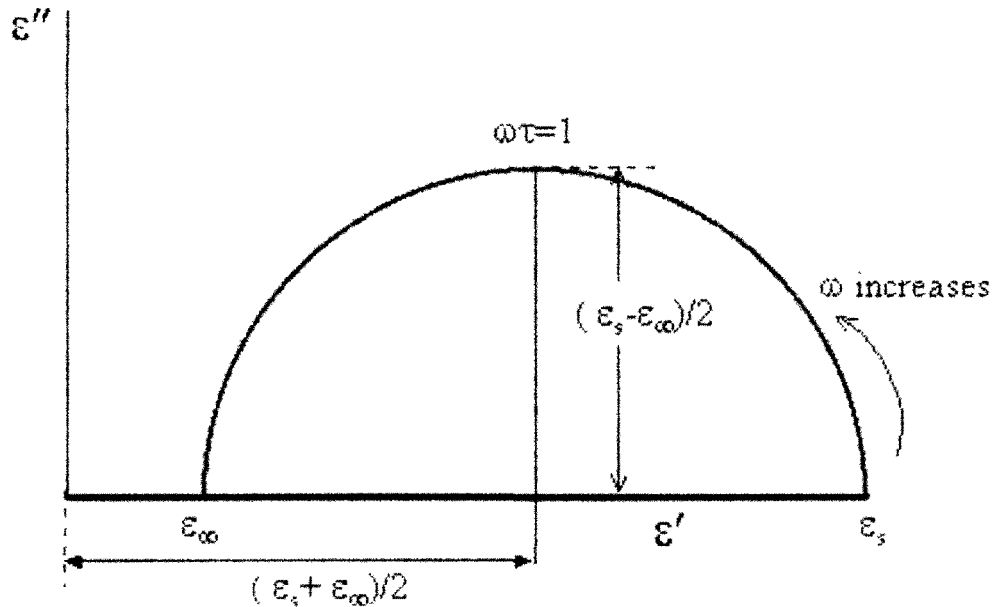


Fig. 3.6 Cole-Cole diagram displaying a semi-circle for Debye equations for  $\epsilon^*$ .

In a given material the measured values of  $\epsilon''$  are plotted as a function of  $\epsilon'$  at various frequencies, usually from  $\omega = 0$  to  $\omega = 10^{10}$  rad/s. If the points fall on a semi-circle we can conclude that the material exhibits Debye relaxation. A Cole-Cole diagram can then be used to obtain the complex dielectric constant at intermediate frequencies obviating the necessity for making measurements. In practice very few materials completely agree with Debye equations, the discrepancy being attributed to what is generally referred to as **distribution of relaxation times**.

The simple theory of Debye assumes that the molecules are spherical in shape and therefore the axis of rotation of the molecule in an external field has no influence in deciding the value of  $\epsilon^*$ . This is more an exception than a rule because not only the molecules can have different shapes, they have, particularly in long chain polymers, a linear configuration. Further, in the solid phase the dipoles are more likely to be interactive and not independent in their response to the alternating field<sup>7</sup>. The relaxation times in such materials have different values depending upon the axis of rotation and, as a result, the dispersion commonly occurs over a wider frequency range.

### 3.6 COLE-COLE RELAXATION

Polar dielectrics that have more than one relaxation time do not satisfy Debye equations. They show a maximum value of  $\epsilon''$  that will be lower than that predicted by equation (3.34). The curve of  $\tan \delta$  vs  $\log \omega\tau$  also shows a broad maximum, the maximum value being smaller than that given by equation (3.37). Under these conditions the plot  $\epsilon''$  vs.  $\epsilon'$  will be distorted and Cole-Cole showed that the plot will still be a semi-circle with its center displaced below the  $\epsilon'$  axis. They suggested an empirical equation for the complex dielectric constant as

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (j\omega\tau_{c-c})^{1-\alpha}}; 0 \leq \alpha \leq 1; \quad (3.45)$$

$\alpha = 0$  for Debye relaxation

where  $\tau_{c-c}$  is the mean relaxation time and  $\alpha$  is a constant for a given material, having a value  $0 \leq \alpha \leq 1$ . A plot of equation (3.45) is shown in figs. (3.7) and (3.8) for various values of  $\alpha$ . Debye equations are also plotted for the purpose of comparison. Near relaxation frequencies Cole-Cole relaxation shows that  $\epsilon'$  decreases more slowly with  $\omega$  than the Debye relaxation. With increasing  $\alpha$  the loss factor  $\epsilon''$  is broader than the Debye relaxation and the peak value,  $\epsilon_{\max}$  is smaller.

A dielectric that has a single relaxation time,  $\alpha = 0$  in this case, equation (3.45) becomes identical with equation (3.29). The larger the value of  $\alpha$ , the larger the distribution of relaxation times.

To determine the geometrical interpretation of equation (3.45) we substitute  $1-\alpha = n$  and rewrite it as

$$\epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (\omega\tau_{c-c})^n (\cos \frac{n\pi}{2} + j \sin \frac{n\pi}{2})} \quad (3.46)$$

Equating real and imaginary parts we get

$$\varepsilon' = \varepsilon_{\infty} + (\varepsilon_s - \varepsilon_{\infty}) \frac{1 + (\omega\tau_{c-c})^n \cos(\frac{n\pi}{2})}{1 + 2(\omega\tau_{c-c})^n \cos(\frac{n\pi}{2}) + (\omega\tau_{c-c})^{2n}} \quad (3.47)$$

$$\varepsilon'' = (\varepsilon_s - \varepsilon_{\infty}) \frac{(\omega\tau_{c-c})^n \sin(n\pi/2)}{1 + 2(\omega\tau_{c-c})^n \cos(n\pi/2) + (\omega\tau_{c-c})^{2n}} \quad (3.48)$$

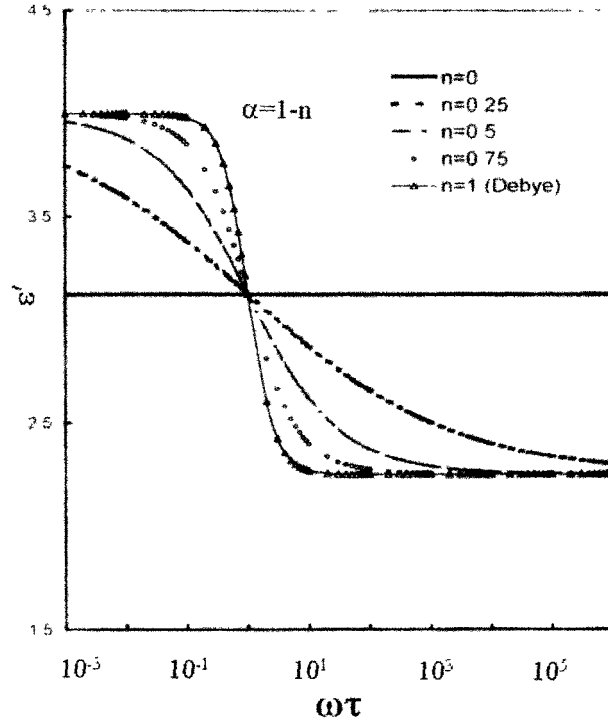


Fig. 3.7 Real part of  $\varepsilon^*$  in a polar dielectric according to Cole-Cole relaxation.  $\alpha = 0$  gives Debye relaxation.

Using the identity

$$j^\alpha \equiv e^{j\alpha\pi/2} \equiv \cos \alpha\pi/2 + j \sin \alpha\pi/2$$

equations (3.47) and (3.48) may be expressed alternatively as<sup>8</sup>

$$\frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_s - \varepsilon_{\infty}} = \frac{1}{2} \left( 1 - \frac{\sinh ns}{\cosh ns + \sin(\alpha\pi/2)} \right) \quad (3.46a)$$

$$\frac{\varepsilon''}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{2} \left( \frac{\cos(\alpha\pi/2)}{\cosh ns + \sin(\alpha\pi/2)} \right) \quad (3.47a)$$

where

$$s = Ln\omega\tau$$

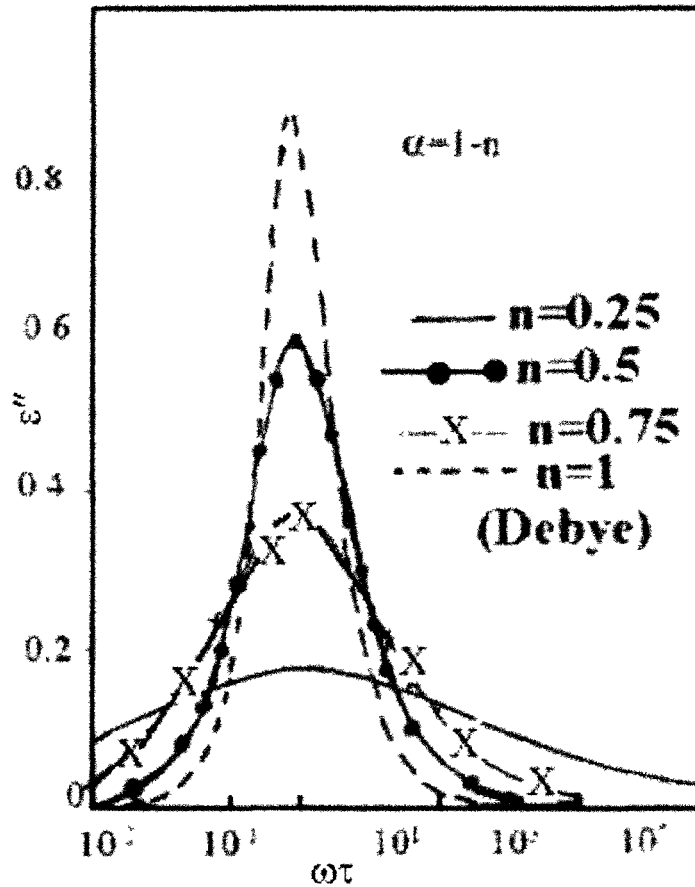


Fig. 3.8 Imaginary part of  $\varepsilon^*$  in a polar dielectric according to Cole-Cole relaxation.  $\alpha = 0$  gives Debye relaxation.

Eliminating  $\omega\tau_{c-c}$  from equations (3.47) and (3.48) Cole-Cole showed that

$$\left( \varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2} \right)^2 + \left[ \varepsilon'' + \frac{\varepsilon_s - \varepsilon_\infty}{2} \cot(n\pi/2) \right]^2 = \left[ \frac{\varepsilon_s - \varepsilon_\infty}{2} \operatorname{cosec}(n\pi/2) \right]^2 \quad (3.49)$$

Equation (3.49) represents the equation of a circle with the center at

$$\left[ \frac{\epsilon_s + \epsilon_\infty}{2}, \frac{\epsilon_\infty - \epsilon_s}{2} \cot(n\pi/2) \right]$$

and having a radius of

$$\left[ \frac{\epsilon_s - \epsilon_\infty}{2} \operatorname{cosec}(n\pi/2) \right]$$

We note that the y coordinate of the center is negative, that is, the center lies below the  $\epsilon'$  axis (fig. 3.9).

Figs. 3.7 and 3.8 show the variation of  $\epsilon'$  and  $\epsilon''$  as a function of  $\omega\tau$  for several values of  $\alpha$  respectively. These are the plots of equations (3.47) and (3.48). At  $\omega\tau = 1$  the following relations hold:

$$\epsilon' = \frac{\epsilon_s + \epsilon_\infty}{2}; \quad \epsilon'' = \frac{\epsilon_s - \epsilon_\infty}{2} \tan \frac{n\pi}{2}$$

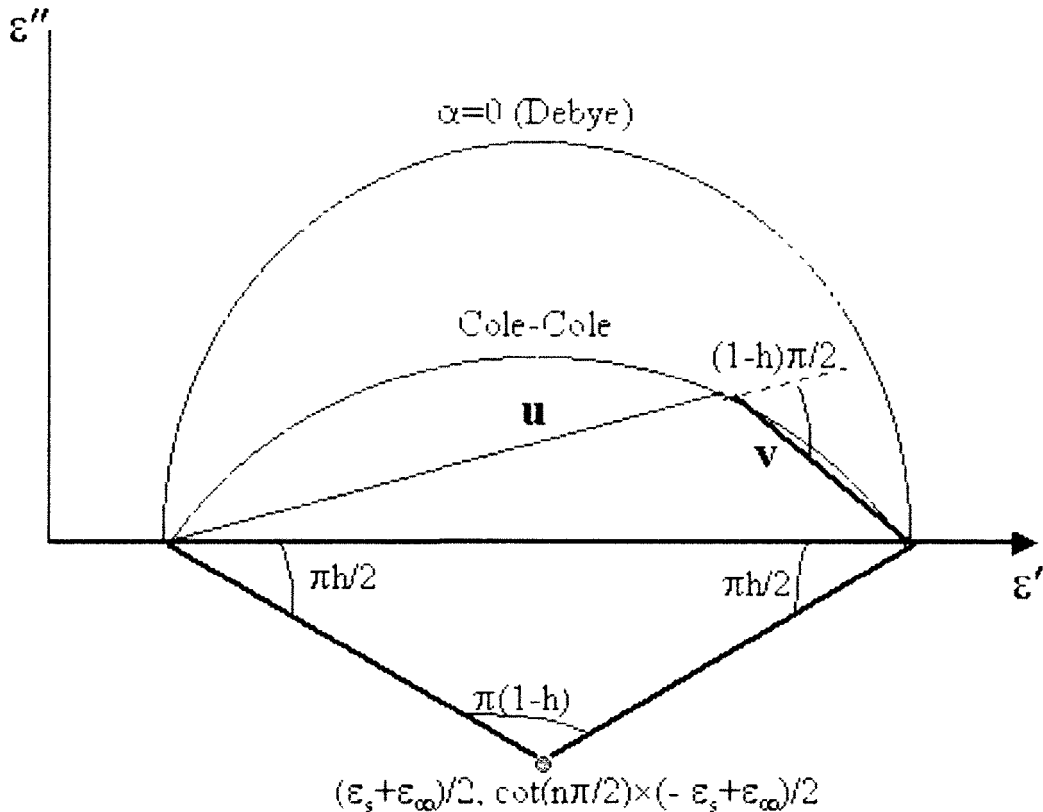


Fig. 3.9 Geometrical relationships in Cole-Cole equation (3.45).

As stated above, the case of  $n = 0$  corresponds to an infinitely large number of distributed relaxation times and the behavior of the material is identical to that under dc fields except that the dielectric constant is reduced to  $(\epsilon_s - \epsilon_\infty)/2$ . The complex part of the dielectric constant is also equal to zero at this value of  $n$ , consistent with dc fields. As the value of  $n$  increases  $\epsilon'$  changes with increasing  $\omega\tau$ , the curves crossing over at  $\omega\tau = 1$ . At  $n=1$  the change in  $\epsilon'$  with increasing  $\omega\tau$  is identical to the Debye relaxation, the material then possessing a single relaxation time.

The variation of  $\epsilon''$  with  $\omega\tau$  is also dependent on the value of  $n$ . As the value of  $n$  increases the curves become narrower and the peak value increases. This behavior is consistent with that shown in fig. 3.8.

Let the lines joining any point on the Cole-Cole diagram to the points corresponding to  $\epsilon_\infty$  and  $\epsilon_s$  be denoted by  $u$  and  $v$  respectively (Fig. 3.9). Then, at any frequency the following relations hold:

$$u = \epsilon^* - \epsilon_\infty; \quad v = \frac{\epsilon^* - \epsilon_\infty}{(\omega\tau)^{1-n}}; \quad \frac{v}{u} = (\omega\tau)^{1-n}$$

By plotting  $\log \omega$  against  $(\log v - \log u)$  the value of  $n$  may be determined. With increasing value of  $n$ , the number of degrees of freedom for rotation of the molecules decreases. Further decreasing the temperature of the material leads to an increase in the value of the parameter  $n$ .

The Cole-Cole diagrams for poly(vinyl chloride) at various temperatures are shown in fig. 3.10<sup>9</sup>. The Cole-Cole arc is symmetrical about a line through the center parallel to the  $\epsilon''$  axis.

### **3.7 DIELECTRIC PROPERTIES OF WATER**

Debye relaxation is generally limited to weak solutions of polar liquids in non-polar solvents. Water in liquid state comes closest to exhibiting Debye relaxation and its dielectric properties are interesting because it has a simple molecular structure. One is fascinated by the fact that it occurs naturally and without it life is not sustained. Hasted (1973) quotes over thirty determinations of static dielectric constant of water, already referred to in chapter 2.

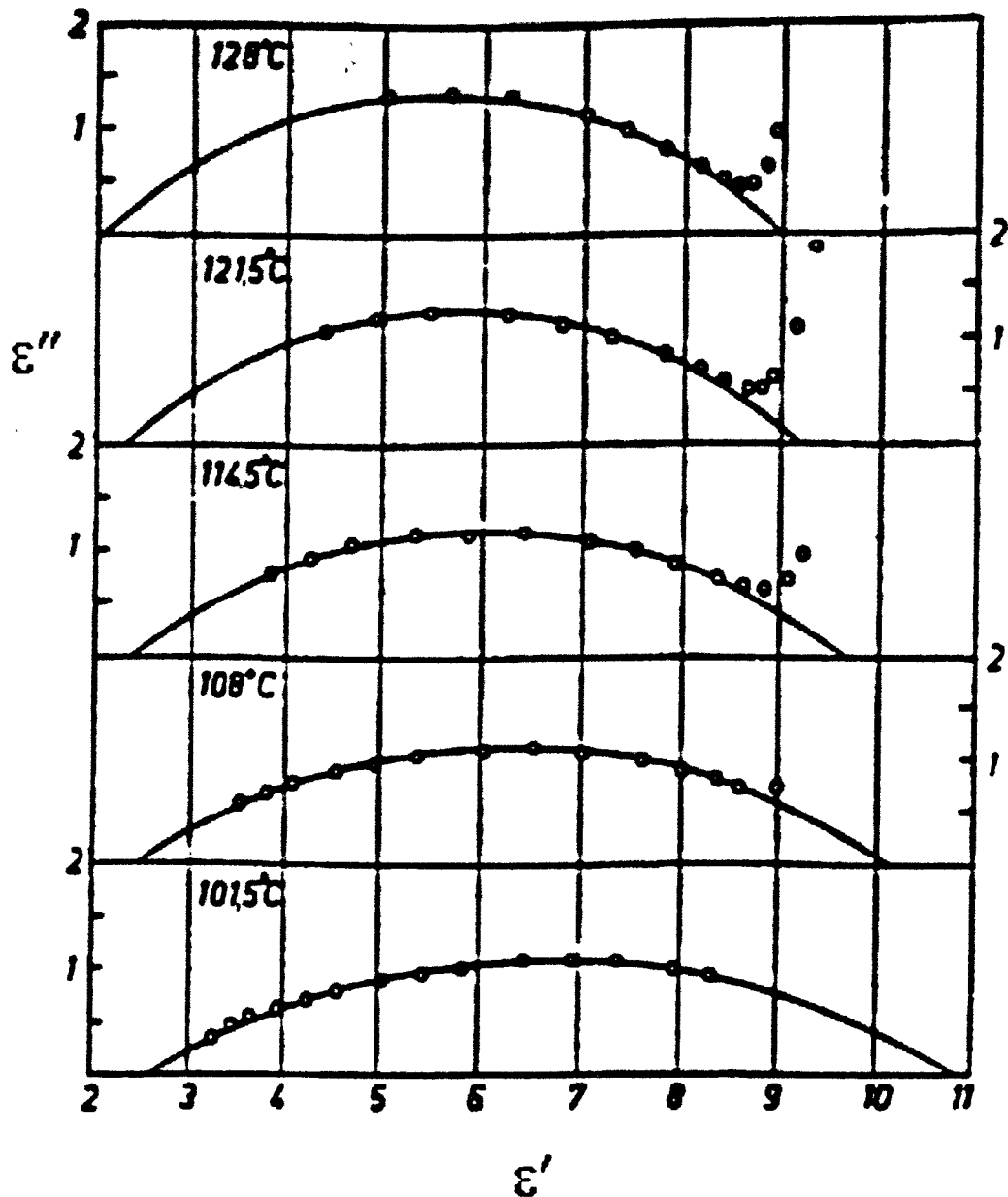


Fig. 3.10 Cole-Cole diagram from measurements on poly (vinyl chloride) at various temperatures (Ishida, 1960). (With permission of Dr. Dietrich Steinkopff Verlag, Darmstadt, Germany).

The dielectric constant is not appreciably dependent on the frequency up to 100 MHz. The measurements are carried out in the microwave frequency range to determine the relaxation frequency, and a particular disadvantage of the microwave frequency is that individual observers are forced, due to cost, to limit their studies to a narrow frequency range. Table 3.1 summarizes the data due to Bottreau et. al. (1975).

**Table 3.1**

Selective Dielectric Properties of Water at 293 K (Bottreau, et. al., 1975).

$$\epsilon_{\infty} = n^2 = 1.78, \epsilon_s = 80.4$$

(With permission of Journal of Chemical Physics, USA)

| $f(\text{GHz})$                                            | Measured complex permittivity |              | Measured reduced permittivity |         | Calculated reduced permittivity |         |
|------------------------------------------------------------|-------------------------------|--------------|-------------------------------|---------|---------------------------------|---------|
|                                                            | $\epsilon'$                   | $\epsilon''$ | $E_m'$                        | $E_m''$ | $E_c'$                          | $E_c''$ |
| 2530.00                                                    | 3.65                          | 1.35         | 0.0238                        | 0.0172  | 0.0230                          | 0.0234  |
| 890.00                                                     | 4.30                          | 2.28         | 0.0321                        | 0.0290  | 0.0335                          | 0.0272  |
| 300.00                                                     | 5.48                          | 4.40         | 0.0471                        | 0.0560  | 0.0384                          | 0.0582  |
| 35.25                                                      | 20.30                         | 29.30        | 0.2356                        | 0.3727  | 0.2230                          | 0.3764  |
| 34.88                                                      | 19.20                         | 30.30        | 0.2216                        | 0.3854  | 0.2262                          | 0.3787  |
| 24.19                                                      | 29.64                         | 35.18        | 0.3544                        | 0.4475  | 0.3600                          | 0.4478  |
| 23.81                                                      | 30.50                         | 35.00        | 0.3653                        | 0.4452  | 0.3667                          | 0.4500  |
| 23.77                                                      | 31.00                         | 35.70        | 0.3717                        | 0.4541  | 0.3674                          | 0.4502  |
| 23.68                                                      | 31.00                         | 35.00        | 0.3717                        | 0.4452  | 0.3690                          | 0.4507  |
| 23.62                                                      | 30.88                         | 35.75        | 0.3701                        | 0.4547  | 0.3701                          | 0.4510  |
| 15.413                                                     | 46.00                         | 36.60        | 0.5625                        | 0.4655  | 0.5645                          | 0.4683  |
| 9.455                                                      | 63.00                         | 31.90        | 0.7787                        | 0.4057  | 0.7618                          | 0.4003  |
| 9.390                                                      | 61.50                         | 31.60        | 0.7596                        | 0.4019  | 0.7641                          | 0.3989  |
| 9.375                                                      | 62.00                         | 32.00        | 0.7660                        | 0.4070  | 0.7646                          | 0.3986  |
| 9.368                                                      | 62.80                         | 31.50        | 0.7761                        | 0.4007  | 0.7649                          | 0.3984  |
| 9.346                                                      | 61.41                         | 31.83        | 0.7585                        | 0.4049  | 0.7656                          | 0.3980  |
| 9.346                                                      | 62.26                         | 32.56        | 0.7693                        | 0.4141  | 0.7656                          | 0.3980  |
| 9.141                                                      | 63.00                         | 31.50        | 0.7787                        | 0.4007  | 0.7728                          | 0.3934  |
| 4.630                                                      | 74.00                         | 18.80        | 0.9186                        | 0.2391  | 0.9215                          | 0.2472  |
| 3.624                                                      | 77.60                         | 16.30        | 0.9644                        | 0.2073  | 0.9486                          | 0.2016  |
| 3.254                                                      | 77.80                         | 13.90        | 0.9669                        | 0.1768  | 0.9576                          | 0.1835  |
| 1.744                                                      | 79.20                         | 7.90         | 0.9847                        | 0.1005  | 0.9868                          | 0.1030  |
| 1.200                                                      | 80.4                          | 7.00         | 1.000                         | 0.0890  | 0.9936                          | 0.0717  |
| 0.577                                                      | 80.3                          | 2.75         | 0.9987                        | 0.0350  | 0.9985                          | 0.0348  |
| Extrapolated values from a single relaxation of Debye type |                               |              |                               |         |                                 |         |
| 13760                                                      | 1.98                          | 0.75         | 0.0026                        | 0.0095  | 0.0021                          | 0.0096  |
| 6880                                                       | 2.37                          | 1.15         | 0.0077                        | 0.0146  | 0.0071                          | 0.0167  |
| 3440                                                       | 3.25                          | 1.45         | 0.0188                        | 0.0184  | 0.0179                          | 0.0227  |

The following definitions apply for the quantities in shown Table 3.1.

$$\epsilon^* = \epsilon' - j\epsilon''; \quad E_m^* = E_m' - jE_m'' = \frac{\epsilon^* - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}};$$

$$E^* = \sum_{i=1}^3 C_i \left(1 + j \frac{f}{f_i}\right) = E_c' - jE_c''$$



and is reproduced from ref.<sup>10</sup>. Fig. 3.11 shows the complex plane plots of  $\epsilon' - j\epsilon''$  for water (Hasted, 1973) and compared with analysis according to Debye equations and Cole-Cole equations. The relaxation time obtained as a function of temperature from Cole-Cole analysis is shown in Table 3.2 along with  $\epsilon_\infty$  used in the analysis.

**Table 3.2**  
Relaxation time in water (Hasted, 1973)

| T° C | $\epsilon_{\infty}$ | $\tau$ ( $10^{-11}$ ) s | $\alpha$ |
|------|---------------------|-------------------------|----------|
| 0    | $4.46 \pm 0.17$     | 1.79                    | 0.014    |
| 10   | $4.10 \pm 0.15$     | 1.26                    | 0.014    |
| 20   | $4.23 \pm 0.16$     | 0.93                    | 0.013    |
| 30   | $4.20 \pm 0.16$     | 0.72                    | 0.012    |
| 40   | $4.16 \pm 0.15$     | 0.58                    | 0.009    |
| 50   | $4.13 \pm 0.15$     | 0.48                    | 0.013    |
| 60   | $4.21 \pm 0.16$     | 0.39                    | 0.011    |
| 75   | $4.49 \pm 0.17$     | 0.32                    | -        |

(permission of Chapman and Hall)

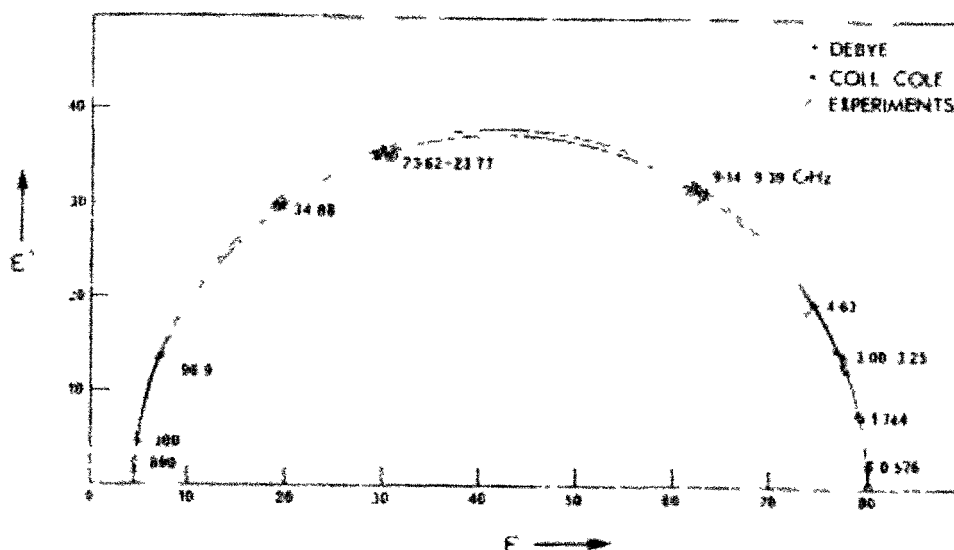


Fig. 3.11 Complex plane plot of  $\epsilon^*$  in water at 25°C in the microwave frequency range. Points in closed circles are experimental data.  $\times$ , calculations from Cole-Cole plot, +, calculations from Debye equation with optimized parameters [Hasted 1973]. (with permission of Chapman & Hall, London).

Earlier literature on  $\epsilon^*$  in water did not extend to as high frequencies as shown in Table 3.1 and it was thought that  $\epsilon_\infty$  is much greater than the square of refractive index,  $n^2 = 1.8$  (Hasted, 1973), and this was attributed to, possibly absorption and a second dipolar dispersion of  $\epsilon''$  at higher frequencies. However more recent measurements up to 2530 GHz and extrapolation to 13760 GHz shows that the equation  $\epsilon_\infty = n^2$  is valid, as demonstrated in Table 3.1. The relaxation time increases with decreasing temperature in qualitative agreement with the Debye concept. The Cole-Cole parameter  $\alpha$  is relatively small and independent of temperature. Recall that as  $\alpha \rightarrow 0$  the Cole-Cole distribution converges to Debye relaxation.

At this point it is appropriate to introduce the concept of spectral decomposition of the complex plane plot of  $\epsilon^*$ . If we suppose that there exist several relaxation processes, each with a characteristic relaxation time and dominant over a specific frequency range, then the Debye equation (3.31) may be expressed as

$$\epsilon' = \epsilon_\infty + \sum_{i=1}^{i=n} \frac{\Delta\epsilon_i}{1 + \omega^2 \tau_i^2} \quad (3.50)$$

$$\epsilon'' = \sum_{i=1}^{i=n} \frac{\Delta\epsilon_i}{1 + \omega^2 \tau_i^2} \omega \tau_i \quad (3.51)$$

where  $\Delta\epsilon_i$  and  $\tau_i$  are the individual amplitude of dispersion ( $\epsilon_{\text{low frequency}} - \epsilon_{\text{high frequency}}$ ) and the relaxation time, respectively. The assumption here is that each relaxation process follows the Debye equation independent of other processes.

This kind of representation has been used to find the relaxation times in D<sub>2</sub>O ice<sup>11</sup>. Polycrystalline ice from water has been shown to have a single relaxation time of Debye type at 270 K<sup>12</sup> and the observed distribution of relaxation times at lower temperatures 165-196 K is attributed to physical and chemical impurities<sup>13</sup>. However the D<sub>2</sub>O ice shows a more interesting behavior. Focusing our attention to the point under discussion, namely several relaxation times, fig. 3.12 shows the measured values of  $\epsilon'$  and  $\epsilon''$  in the complex plane as well as the three relaxation processes. The  $\Delta\epsilon$  and  $\tau$  are 88.1, 57.5 and 1.4 (see inset) and, 20 ms, 60 ms and 100  $\mu$ s respectively.

A method of spectral analysis which is similar in principle to what was described above, but different in procedure, has been adopted by Bottreau et. al. (1975) who use a function of the type

$$\varepsilon^* = \sum_{i=1}^n C_i (1 + j \frac{\omega}{\omega_i})^{-1} \quad (3.52)$$

where  $C_i$  is the spectral contribution to  $i^{\text{th}}$  region and  $\omega_i$  is its relaxation frequency. The condition  $\sum C_i = 1$  should be satisfied.

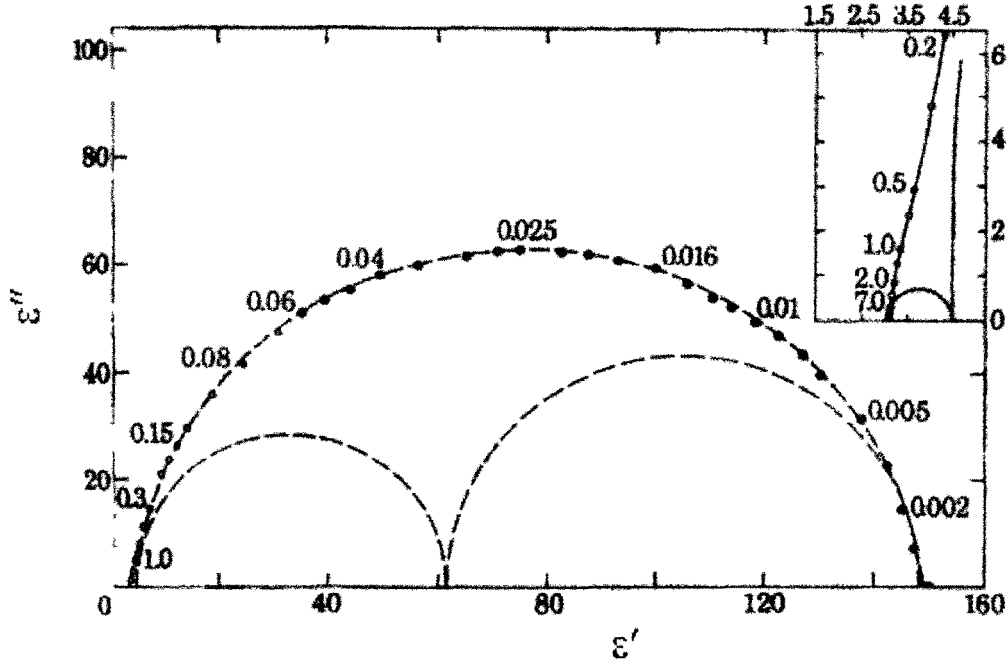


Fig. 3.12 The analysis of Cole-Cole plots into three Debye-type relaxation regions indicated by semi-circles at 191.8 K. The numbers beside the filled data points are frequencies in kHz. Closed circles: low frequency bridge measurements; Open circles: high frequency measurements [11]. (with permission of the Royal Society, England).

This scheme was applied to  $\text{H}_2\text{O}$  data shown in Table 3.1. The results obtained are shown in Table 3.3. Three Debye regions are identified with relaxation times as shown. Application of Cole-Cole relaxation (3.45) equation yields a value of  $\omega_p = 107 \times 10^9 \text{ rad s}^{-1}$  with  $\alpha = 0.013$  which agrees with the major region of relaxation in Table 3.3.

### 3.8 DAVIDSON – COLE EQUATION

Davidson – Cole<sup>14</sup> have suggested the empirical equation

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + j\omega\tau_{d-c})^\beta} \quad (3.53)$$

where  $0 \leq \beta \leq 1$  is a constant characteristic of the material.

Separating the real and imaginary parts of equation (3.53), the real and complex parts are expressed as

$$\varepsilon' - \varepsilon_{\infty} = (\varepsilon_s - \varepsilon_{\infty})(\cos \phi)^{\beta} \cos \phi \beta \quad (3.54)$$

$$\varepsilon'' = (\varepsilon_s - \varepsilon_{\infty})(\cos \phi)^{\beta} \sin \phi \beta \quad (3.55)$$

where  $\tan \phi = \omega \tau_0$ .

**Table 3.3**

Spectral contributions and relaxation frequencies of the three Debye constituents of water at 20° C [Bottreau et. al. 1975].

| Region | $C_i$  | $f_i$ (GHz)      |
|--------|--------|------------------|
| I      | 0.0507 | $5.57 \pm 0.50$  |
| II     | 0.9136 | $17.85 \pm 0.30$ |
| III    | 0.0357 | $3440.3 \pm 8.0$ |

(with permission of J. Chem. Phys.)

These equations are plotted in Figs. 3.13 and 3.14 and the Debye curves ( $\beta = 1$ ) are also shown for comparison. The low frequency part of  $\varepsilon'$  remains unchanged as the value of  $\beta$  increases from 0 to 1. However the high frequency part of  $\varepsilon'$  becomes lower as  $\beta$  is increased,  $\beta = 1$  (Debye) yielding the lowest values.

Similar observations hold good for  $\varepsilon''$  which increases with  $\beta$  in the low frequency part and decreasing with  $\beta$  in the high frequency part. The main point to note is that the curve of  $\varepsilon''$  against  $\omega \tau$  loses symmetry on either side of the line that is parallel to the  $\varepsilon''$  axis and that passes through its peak value.

Expressing equations (3.54) and (3.55) in polar co-ordinates

$$r = [(\varepsilon' - \varepsilon_{\infty})^2 + \varepsilon''^2]$$

$$\theta = \tan^{-1} \frac{\epsilon''}{\epsilon' - \epsilon_\infty}$$

Davidson-Cole show, from equations (3.54) and (3.55) that

$$r = (\epsilon_s - \epsilon_\infty)[(\cos(\theta / \beta)]^\beta \quad (3.56)$$

$$\tan \theta = \tan \beta \phi \quad (3.57)$$

$$\omega \tau_{d-c} = \tan\left(\frac{\theta}{\beta}\right) \quad (3.58)$$

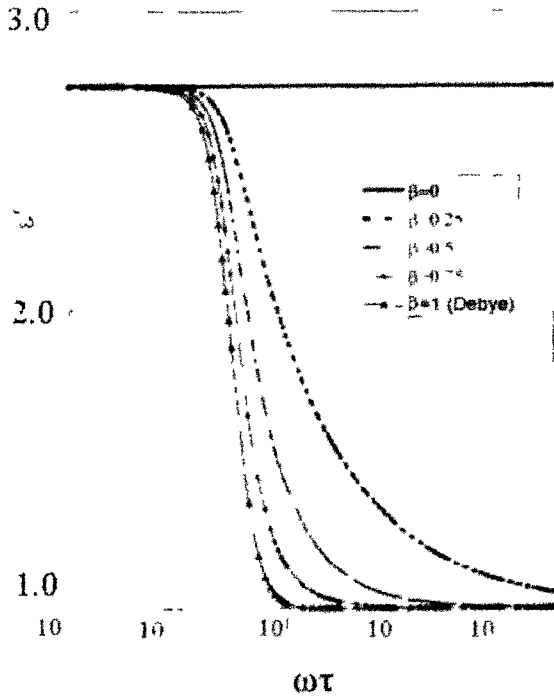


Fig. 3.13 Schematic variation of  $\epsilon'$  as a function of  $\omega\tau$  for various values of  $\beta$ . The low frequency value of  $\epsilon'$  has been arbitrarily chosen.

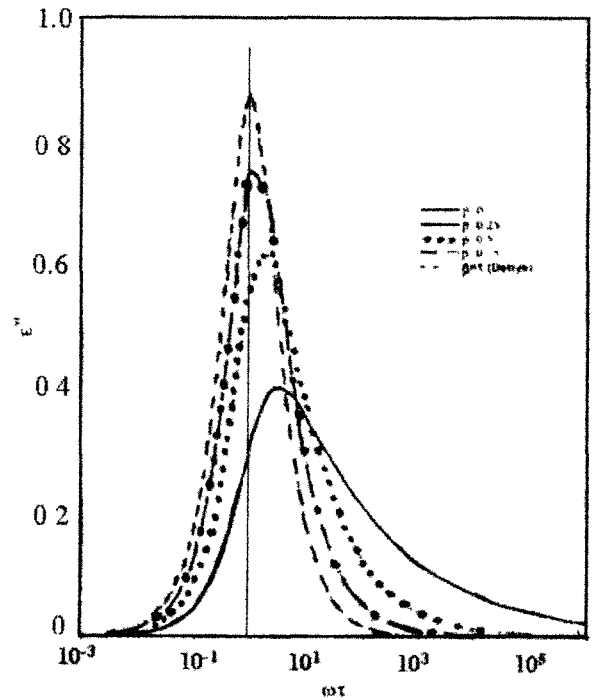


Fig. 3.14 Schematic variation of  $\epsilon''$  as a function of  $\omega\tau$  for various values of  $\beta$ . The value of  $\tau$  has been arbitrarily chosen.

The locus of equation (3.53) in the complex plane is an arc with intercepts on the  $\epsilon'$  axis at  $\epsilon_s$  and  $\epsilon_\infty$  at the low frequency and high frequency ends respectively (fig. 3-15). As  $\omega \rightarrow 0$  the limiting curve is a semicircle with center on the  $\epsilon'$  axis and as  $\omega \rightarrow \infty$  the

limiting straight line makes an angle of  $\beta\pi/2$  with the  $\epsilon'$  axis. To explain it another way, at low frequencies the points lie on a circular arc and at high frequencies they lie on a straight line.

If Davidson-Cole equation holds then the values of  $\epsilon_s$ ,  $\epsilon_\infty$  and  $\beta$  may be determined directly, noting that a plot of the right hand quantity of eq. (3.54) against  $\omega$  must yield a straight line. The frequency  $\omega_p$  corresponding to  $\tan(\theta/\beta) = 1$  may be determined and  $\tau$  may also be determined from the relation  $\omega_p \tau = 1$ . We quote two examples to demonstrate Davidson-Cole relaxation in simple systems. Fig. 3-16 shows the measured loss factor in glycerol (b. p. 143-144°C at 300 Pa), over a wide range of temperature and frequency<sup>15</sup>. The asymmetry about the peak can clearly be seen and in the high frequency range, to the right of the peak at each temperature, a power law,  $\omega^{-\beta}$  ( $\beta < 1$ ) holds true.

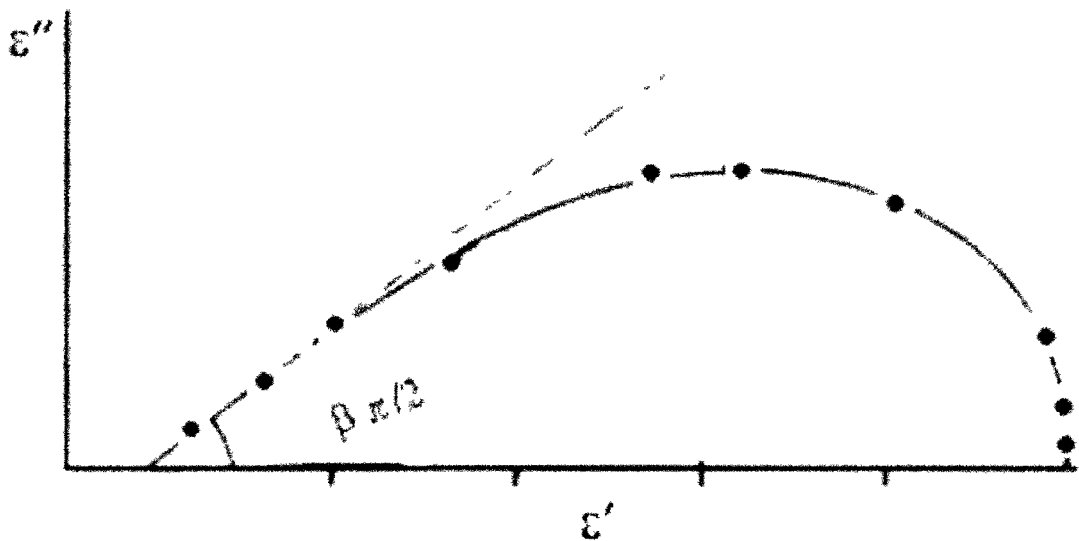


Fig. 3.15 Complex plane plot of  $\epsilon^*$  according to Davidson-Cole relaxation. The loss peak is asymmetric and the low frequency branch is proportional to  $\omega$ . The slope of the high frequency part depends on  $\beta$ .

The second example of Davidson-Cole relaxation is in mixtures of water and ethanol [Bao et. al., 1996] at various fractional contents of each liquid, as shown in fig. 3-17. The Davidson-Cole relaxation is found to hold true though the Debye relaxation may also be applicable if great accuracy is not required. The methods of determining the type of relaxation is dealt with later, but, as noted earlier, the Davidson-Cole relaxation is broader than the Debye relaxation depending upon the value of  $\beta$ .

We need to deal with an additional aspect of the complex plane plot of  $\epsilon^*$  which is due to the fact that conductivity of the dielectric introduces anomalous increase of  $\epsilon''$  at both

the high frequency (see the inset in fig. 3-12) and low frequency ends of the plots<sup>16</sup> (fig. 3.18). Equation (3.8) shows the contribution of ac conductivity to  $\epsilon''$  and this contribution should be subtracted before deciding upon the relaxation mechanisms.

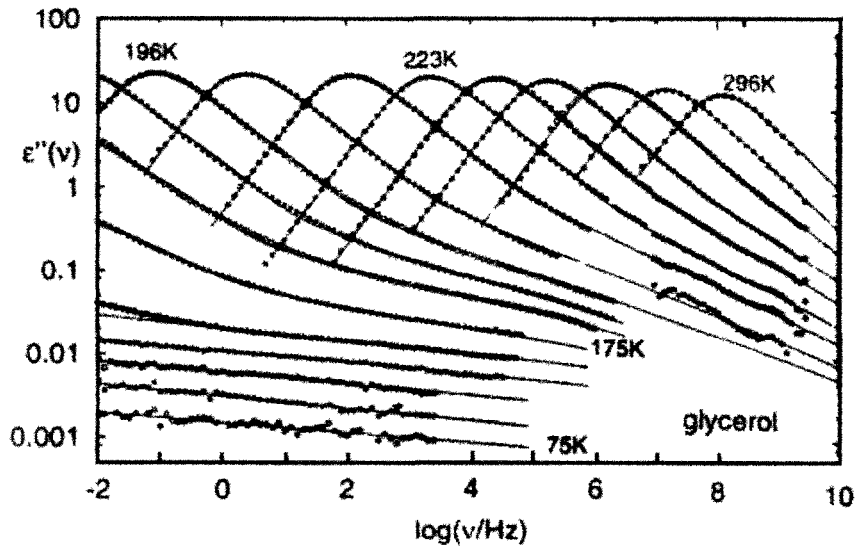


Fig. 3.16  $\epsilon''$  as a function of  $\omega$  in glycerol at various temperatures (75, 95, 115, 135, 175, 185, 190, 196, 203, 213, 223, 241, 256, 273 and 296 K) [15]. (with permission of J. Chem. Phys., USA).

### **3.9 MACROSCOPIC RELAXATION TIME**

The relaxation time is a function of temperature according to a chemical rate process defined by

$$\tau = \tau_0 \exp \frac{b}{kT} \quad (3.59)$$

in which  $\tau_0$  and  $b$  are constants. This is referred to as an Arrhenius equation in the literature.

There is no theoretical basis for dependence of  $\tau$  on  $T$  and in some liquids such as those studied by Davidson and Cole (1951) the relaxation time is expressed as

$$\tau = \tau_0 \exp \frac{b}{k(T - T_c)} \quad (3.60)$$

where  $T_c$  is a characteristic temperature for a particular liquid.

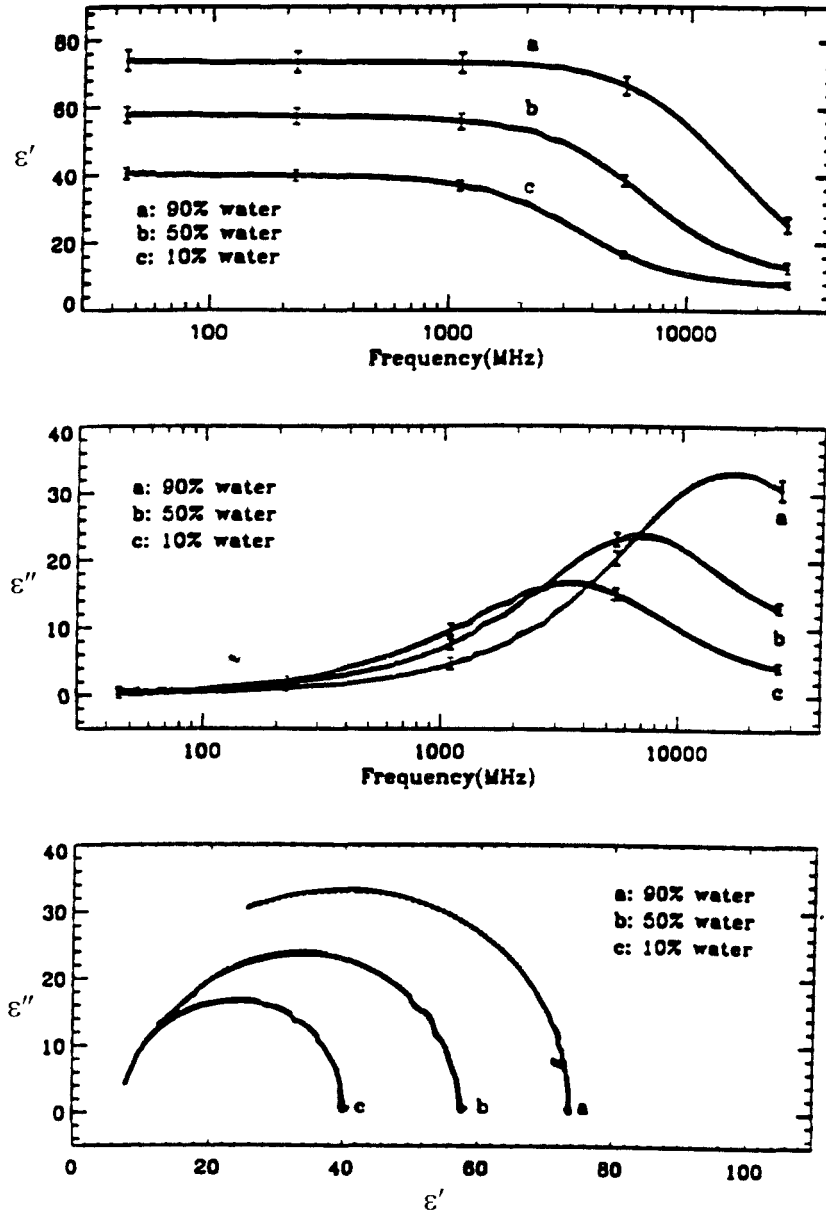


Fig. 3.17 Dielectric properties of water-ethanol mixtures at 25°C. (a) Real part  $\epsilon'$  (b) Imaginary part,  $\epsilon''$  (c) Complex plane plot of  $\epsilon^*$  exhibiting Davidson-Cole relaxation [Bao et. al. 1996] (with permission of American Inst. of Physics).



In some liquids the viscosity and measured low field conductivity also follow a similar law, the former given by

$$\eta = \eta_o \exp \left[ \frac{b_\eta}{k(T - T_c)} \right] \quad (3.61)$$

At  $T = T_c$  the relaxation time is infinity according to equation (3.60) which must be interpreted as meaning that the relaxation process becomes infinitely slow as we approach the characteristic temperature. Fig. 3.19 (Johari and Whalley, 1981) shows the plots of  $\tau$  against the parameter  $1000/T$  in ice. The slope of the line gives an activation energy of 0.58 eV, a further discussion of which is beyond the scope of the book. We will make use of equation (3.60) in understanding the behavior of amorphous polymers near the glass transition temperature  $T_G$  in chapter 5.

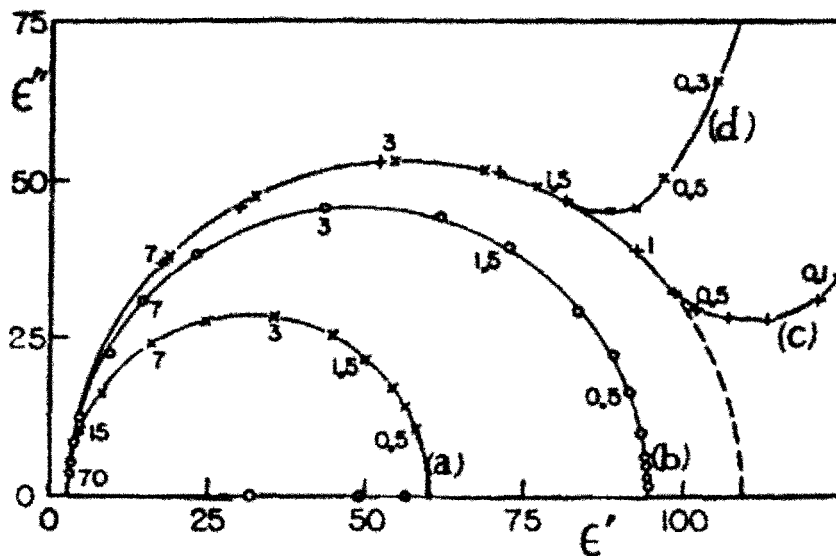


Fig. 3.18 Complex plane plot of  $\epsilon^*$  in ice at 262.2 K. (a) sample with interface parallel to the electrodes; Curve (b), true locus; curves (c) and (d), samples with electrode polarization arising from dc conductance. Numbers beside points are frequencies in kHz (Auty and Cole, 1952). (with permission from Am. Inst. Phys.).

The observed correspondence of  $\tau$  with viscosity is qualitatively in agreement with the molecular relaxation theory of Debye<sup>17</sup> who obtained the equation

$$\tau_m = \frac{3\eta v}{kT} \quad (3.62)$$

where  $\tau_m$  is called the molecular relaxation time (see next section),  $\eta$  the viscosity,  $v$  the molecular volume ( $= 4\pi a^3/3$  where  $a$  is the molecular radius), assumed spherical. The molecular volume required to obtain agreement with the relaxation times is too small for glycerol and propylene glycol ( $\sim 10^{-31} \text{ m}^3$ ) and of reasonable size for *n*-propanol ( $60\text{-}900 \times 10^{-30} \text{ m}^3$ ).

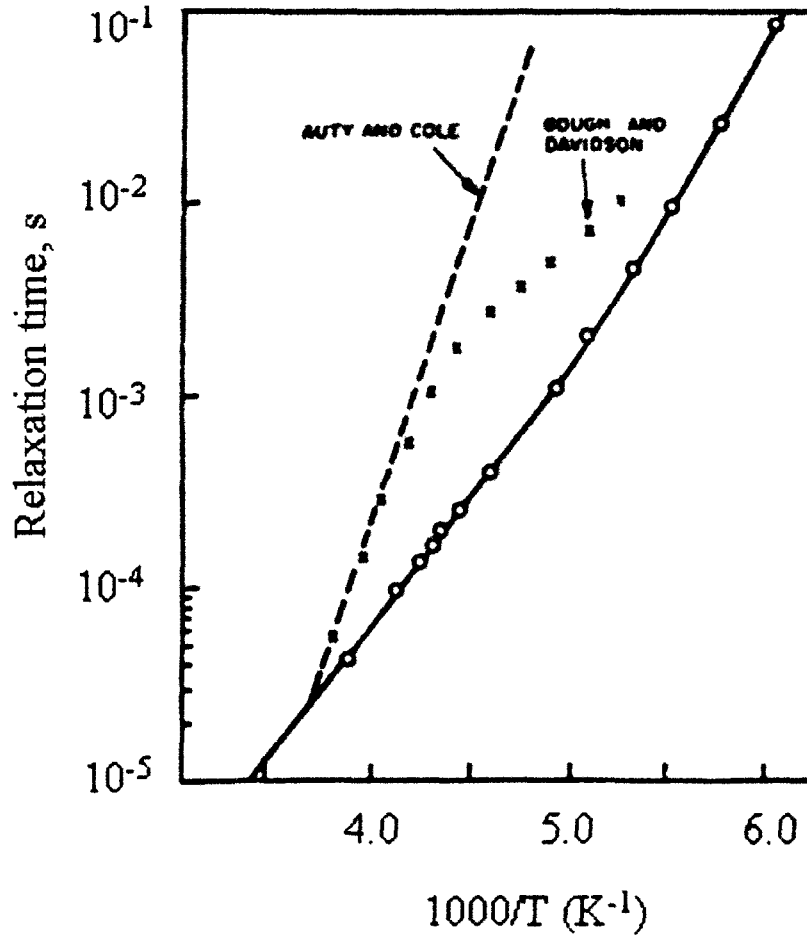


Fig. 3.19 Arrhenius plot of the relaxation time of ice I plotted as a function of  $1/T$  (Johari and Whalley, 1981). (with permission of Am. Inst. Phys.).

The spread in these values arises due to the fact that the molecular relaxation time,  $\tau_D$ , and the relaxation time,  $\tau$ , obtained from the dielectric studies may be related in several ways. The inference is that for the first two liquids the units involved are much smaller

where as for the third named liquid the unit involved may be the entire molecule. These details are included here to demonstrate the method employed to obtain insight into the relaxation mechanism from measurements of dielectric properties.

### **3.10 MOLECULAR RELAXATION TIME**

The relaxation time  $\tau$  obtained from dielectric studies that we have discussed so far is a macroscopic quantity and it is quite different from the original relaxation time  $\tau_m$  used by Debye.  $\tau_m$  is a microscopic quantity and usually called the internal relaxation time or the molecular relaxation time.  $\tau_m$  may be expressed in terms of the viscosity of the liquid and the temperature as

$$\tau_m = \frac{4\pi\eta a^3}{kT} \quad (3.63)$$

where  $a$  is the molecular radius. The molecular relaxation time is assumed to be due to the inner friction of the medium that hinders the rotation of polar molecules. Hence  $\tau_m$  is a function of viscosity. As an example of applicability of equation (3.63) we consider water that has a viscosity of 0.01 Poise at room temperature and an effective molecular radius of  $2.2 \times 10^{-10}$  m leading to a relaxation time of  $2.5 \times 10^{-11}$  s. At relaxation, the condition  $\omega\tau = 1$  is satisfied and therefore  $\omega = 4 \times 10^{10} \text{ s}^{-1}$  which is in reasonable agreement with relaxation time obtained from dielectric studies. Equation (3.63) is however expected to be valid only approximately because the internal friction hindering the rotation of the molecule, which is a molecular parameter, is equated to the viscosity, which is a macroscopic parameter.

It is well known that the viscosity of a liquid varies with the temperature according to an empirical law:

$$\eta \propto \exp \frac{c}{kT} \quad (3.64)$$

in which  $c$  is a constant for a given liquid. Therefore eq. (3.63) may now be expressed as

$$\tau_m \propto \frac{1}{T} \exp \frac{c}{kT} \quad (3.65)$$

The relaxation time increases with decreasing temperature, as found in many substances. (see Table 3.2).

### **3.11 STRAIGHT LINE RELATIONSHIPS**

There are many convenient methods for measuring the relaxation time experimentally and the formulas for calculating  $\tau$  have been summarized by Hill et. al<sup>18</sup>. Let  $\omega\tau = 1$  and  $n^2 = \epsilon_\infty$ . Equation (3.28) and (3.29) may be expressed in several alternative ways:

$$1. \frac{\epsilon' - n^2}{\epsilon_s - n^2} = \frac{1}{1 + x^2}$$

$$\frac{\epsilon''}{\epsilon_s - n^2} = \frac{x}{1 + x^2}$$

Dividing the second equation from the first

$$x = \frac{\epsilon''}{\epsilon' - n^2} \quad (3.66)$$

2. It is easy to show that

$$x = \frac{\epsilon_s - \epsilon'}{\epsilon''}$$

Equation (3.66) shows that a graph of  $\epsilon''/x$  against  $\epsilon'$  will be a straight line. The graph of  $\epsilon''x$  as a function of  $\epsilon'$  will also be linear.  $n^2$  and  $\epsilon_s$  are obtained from the respective intercepts and  $\tau$  from the slope.

The equations may also be written as :

$$3. \quad \frac{x}{\epsilon''} = \frac{x^2}{\epsilon_s - n^2} + \frac{1}{\epsilon_s - n^2}$$

$$4. \quad \frac{1}{\epsilon''x} = \frac{1}{(\epsilon_s - n^2)x^2} + \frac{1}{(\epsilon_s - n^2)}$$

$$5. \quad \frac{1}{\varepsilon' - n^2} = \frac{x^2}{\varepsilon_s - n^2} + \frac{1}{\varepsilon_s - n^2}$$

$$6. \quad \frac{1}{\varepsilon_s - \varepsilon'} = \frac{1}{(\varepsilon_s - n^2)x^2} + \frac{1}{(\varepsilon_s - n^2)}$$

Equations (3)-(6) above have the advantage that they each involve only one of the experimentally measured values of  $\varepsilon'$  and  $\varepsilon''$ , but the disadvantage is that the frequency term,  $x$ , enters through a squared term distorting the frequency scale. The advantage of these relationships lie in the fact that they may be used to check the standard deviation between computed values and measured values using easily available software.

The relation between the molecular relaxation time,  $\tau_m$ , and the macroscopic relaxation time,  $\tau$ , is given by (Hill et. al.)

$$\tau = \frac{\varepsilon_s + 2}{n^2 + 2} \tau_m \quad (3.67)$$

The macroscopic relaxation time is higher in all cases than the microscopic relaxation time.

### **3.12 FROHLICH'S ANALYSIS**

It is advantageous at this point to consider the dynamical treatment of Frohlich<sup>19</sup> who visualized a relaxation time that is dependent upon the temperature according to equation (3.63). To understand Frohlich's model let us take the electric field along the + axis and suppose that the dipole can orient in only two directions; one parallel to the electric field, the other anti-parallel. Let us also assume that the dipole is rigidly attached to a molecule. The energy of the dipole is +w when it is parallel to the field, -w when it is anti-parallel, and zero when it is perpendicular. As the field alternates the dipole rotates from a parallel to the anti-parallel position or vice-versa. Only two positions are allowed. A rotation through 180° is considered as a jump.

Frohlich generalized the model which is based on the concept that the activation energies of dipoles vary between two constant values,  $w_1$  and  $w_2$ . Frohlich assumed that each

process obeyed the Arrhenius relationship and the relaxation times corresponding to  $w_1$  and  $w_2$  are given by

$$\tau_1 = \tau_0 e^{\frac{w_1}{kT}}$$

$$\tau_2 = \tau_0 e^{\frac{w_2}{kT}}$$

The dipoles are distributed uniformly in the energy interval  $dw$  and make a contribution to the dielectric constant according to  $J_\omega$  and  $H_\omega$ . The analysis leads to fairly lengthy expressions in terms of the difference in the activation energy  $w_2 - w_1$ , and the final equations are

$$J_\omega = \frac{\epsilon' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = 1 - \frac{1}{2s} \text{Ln} \left[ \frac{1 + x^2 e^s}{1 + x^2 e^{-s}} \right]$$

$$H_\omega = \frac{\epsilon''}{\epsilon_s - \epsilon_\infty} = \frac{1}{s} (e^{\frac{s}{2}} \tan^{-1} x - e^{-\frac{s}{2}} \tan^{-1} x) \quad (3.68)$$

where

$$s = \frac{w_2 - w_1}{kT}; \quad x = \frac{\omega_p}{\omega}$$

We have used here the form of expressions given by Williams<sup>20</sup> because they have the advantage of using  $\omega_p$  which is the radian frequency at which  $\epsilon''$  is a maximum. Since  $s$  is a function of temperature the shape of the  $J_\omega$  and  $H_\omega$  curves will vary with temperature, tending towards a single relaxation time at higher temperatures.  $\omega_p$  is related to  $\tau_1$  and  $\tau_2$ ,

$$\omega_p = \frac{1}{\tau_1} e^{\frac{-(w_2 - w_1)}{2kT}} = \frac{1}{\sqrt{\tau_1 \tau_2}}$$

Fig. 3.20 shows the factor  $\epsilon''/\epsilon''_{\max}$  as a function of  $\omega/\omega_p$  calculated according to

$$\frac{\varepsilon''}{\varepsilon''_m} = \frac{(\tan^{-1} \frac{\omega}{\omega_p}) \sqrt{\frac{\tau_2}{\tau_1}} - (\tan^{-1} \frac{\omega}{\omega_p}) \sqrt{\frac{\tau_1}{\tau_2}}}{\tan^{-1} \sqrt{\frac{\tau_2}{\tau_1}} - \tan^{-1} \sqrt{\frac{\tau_1}{\tau_2}}} \quad (3.69)$$

The width of the loss curve increases with increasing  $(w_2 - w_1)$ , and in the limit the relaxation time will vary from zero to infinity and  $\varepsilon''$  will have a constant value over the entire frequency range.

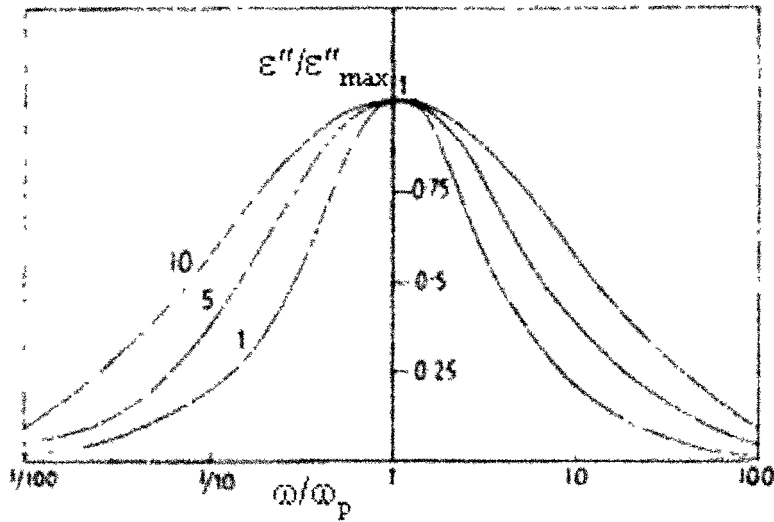


Fig. 3.20 Dependence of dielectric loss  $\varepsilon''(\omega)$  on  $\omega$  according to equation (3.69) for three values of the parameter  $\sqrt{(\tau_2/\tau_1)} = 1, 5, 10$ . They correspond to a range of heights of the potential barrier.  $\omega_p$  is the frequency of  $\varepsilon''_{\max}$  [1986]. (with permission of Clarendon Press, Oxford.)

The double potential well of Frohlich leads to a relaxation function that shows the peak of the  $\varepsilon'' - \omega$  plots are independent of the temperature. However, measurements of  $\varepsilon''$  in a wide range of materials show that the peak increases with increase in  $T$ . For example measurement of dielectric loss in polyimide having adsorbed water shows such a behavior<sup>21</sup>.

The temperature dependence of  $\varepsilon''_{\max}$  in the context of Frohlich's theory is often explained by assuming asymmetry in the energy level of the two positions of the dipole. At lower temperatures the lower well is occupied and the higher well remains empty. The number of dipoles jumping from the lower to higher well is zero. However, with increasing temperature the number of dipoles in the higher well increases until both wells

are occupied equally at  $kT \gg (w_2 - w_1)$ . Therefore there will be a temperature range, depending upon the energy difference, in which  $\varepsilon''$  increases strongly. According to this model the loss factor is

$$\varepsilon'' \propto \frac{1}{3kT} \cosh^{-2} \left[ \frac{w_1 - w_2}{2kT} \right] = f(T)$$

where  $(w_2 - w_1)$  is the difference in the asymmetry of the two positions. Plots of  $f(T)$  versus  $T$  for various values of  $V$  are shown in the range of  $V = 0$  to  $100$  meV (fig. 3.21). By comparing the observed variation of  $\varepsilon''$  vs  $T$  it is possible to estimate the average energy of asymmetry between the two wells.

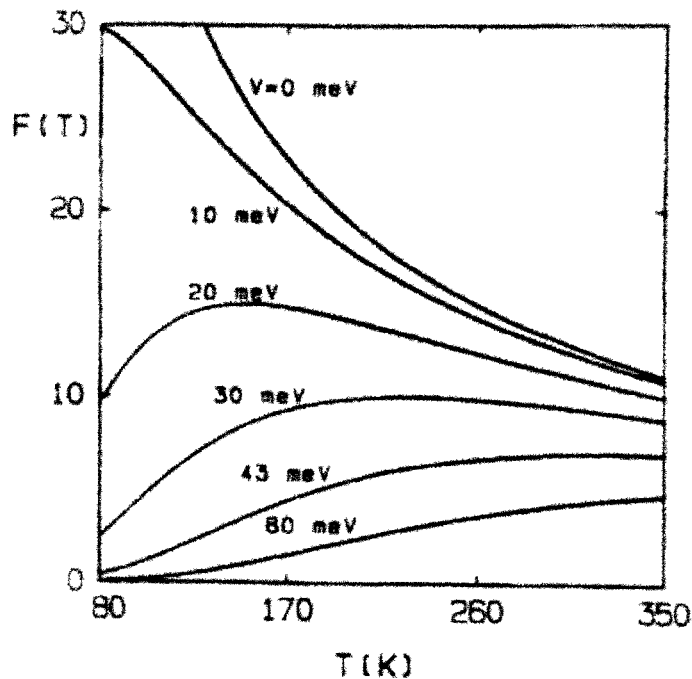


Fig. 3.21 Temperature dependance of the relaxation strength calculated for various values of the asymmetry potential  $w_1 - w_2$ . The upper curve corresponds to the symmetric case  $w_1 - w_2 = 0$  (Melcher et. al., 1989). (with permission of Trans. IEEE on Diel. and El. Insul.)

### 3.13 FUOSS-KIRKWOOD EQUATION

The Fuoss-Kirkwood<sup>22</sup> dispersion equation is



$$\varepsilon'' = \varepsilon_{\infty} + (\varepsilon_s - \varepsilon_{\infty})\delta \frac{(\omega\tau)^{\delta}}{1 + (\omega\tau)^{2\delta}} \quad (3.70)$$

Let us denote the frequency at which the loss factor is a maximum for Debye relaxation by  $\omega_p$ . Then the loss factor in terms of its maximum value,  $\varepsilon''_{\max}$ , is

$$\varepsilon'' = \frac{2\varepsilon''_{\max}}{\frac{\omega}{\omega_p} + \frac{\omega_p}{\omega}}$$

which leads to

$$\varepsilon'' = \varepsilon''_{\max} \operatorname{sech}\left(Ln \frac{\omega}{\omega_p}\right)$$

In the Fuoss-Kirkwood derivation this expression becomes

$$\varepsilon'' = \varepsilon''_{\max} \operatorname{sech}\left(\delta Ln \frac{\omega}{\omega_p}\right)$$

The empirical factor  $\delta$ , between 0 and 1, is related to the Cole-Cole parameter  $\alpha$  according to

$$\delta\sqrt{2} = \frac{1 - \alpha}{\cos \frac{(1 - \alpha)\pi}{4}}$$

This expression shows that Fuoss-Kirkwood relation holds true for most materials in which the Cole-Cole relaxation is observed; only the value of the parameter will be different.

When  $\varepsilon'' = 1/2 \varepsilon''_{\max}$  expression (3.70) leads to  $(\omega\tau)^{\delta} = 2 \pm \sqrt{3}$ . To apply Fuoss-Kirkwood equation we plot  $\operatorname{arccosh}(\varepsilon''/\varepsilon')$  against  $(\ln\omega)$  to get a straight line. This line intersects the frequency axis at  $\omega = \omega_p$  with a slope of  $\delta$  which is related to the static permittivity in accordance with<sup>23</sup>

$$\delta = \frac{2\varepsilon''_{\max}}{\varepsilon_s - \varepsilon_{\infty}}$$

Fig. 3.22 shows such a plot for PMMA at 353K and the evaluated parameter  $(\varepsilon_s - \varepsilon_{\infty})$  has value of  $\cong 2$ .

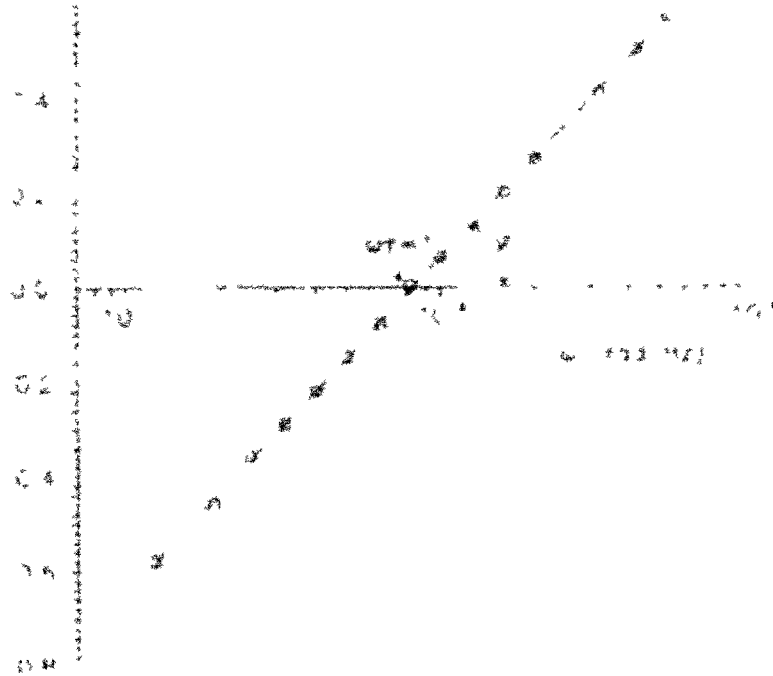


Fig. 3.22 The dependence of  $\text{arccosh}(\varepsilon''_{\max}/\varepsilon'')$  on  $\log(\omega)$  for PMMA at 353 K.  $\tau$  is the relaxation time. Slope gives the value of  $\beta$ . From the slope  $(\varepsilon_s - \varepsilon_{\infty})$  is evaluated as  $\cong 2$  [Mazur, 1997]. (with permission of Institute of Physics).

Kirkwood and Fuoss<sup>24</sup> also derived the relaxation time distribution function for a freely jointed polyvinyl chloride (PVC) chain, including the molecular weight distribution. Recall that the number of monomer units in a polymer molecule is not a constant and shows a distribution. The theory takes into account the hydrodynamic diffusion of chain segments under an electric field (Williams, 1963). Polyvinyl chloride and poly(acetaldehyde) show common characteristics of the dipole forming a rigid part of the chain backbone. The Kirkwood-Fuoss relation is

$$J_{\omega} - jH_{\omega} = \int_0^{\infty} \frac{[1 + u + u(u + 2)e^u Ei(-u)][1 - jxu]du}{1 + x^2 u^2} \quad (3.71)$$

here  $u = n / \langle n \rangle$ ,  $n$  is the degree of polymerization,  $\langle n \rangle$  its average value,  $Ei(u)$  the exponential integral,  $x = \langle n \rangle \omega \tau^*$ ,  $\tau^*$  is the relaxation time of the monomer unit.  $H_{\omega}$  reaches its peak value at  $x = 0.1 \times 2\pi$  and is symmetrical about this value. The main feature of Kirkwood-Fuoss distribution is that it is free of any empirical parameter because  $J_{\omega}$  and  $H_{\omega}$  are expressed in terms of  $\log x$ .

The shape and height of no-parameter distribution of Kirkwood-Fuoss is independent of temperature and this fact explains the reason for their theory not holding true for PVC. The distribution in PVC is markedly temperature dependent (Kirk and Fuoss, 1941).

Many polymers exhibit a temperature dependent distribution and at higher temperatures some are noticeably temperature independent. At these higher temperatures the Cole-Cole parameter has an approximate value of 0.63 (Kirkwood and Fuoss, 1941). It seems likely that the Kirkwood-Fuoss relation holds when the shape of the distribution is independent of the temperature.

### **3.14 HAVRILIAK AND NEGAMI DISPERSION**

We are now in a position to extend our treatment to more complicated molecular structures, in particular polymer materials. The dispersion in small organic or inorganic molecules is studied by measuring the complex dielectric constant of the material at constant temperature over as wide a range of frequency as possible. The temperature is then varied and the measurements repeated till the desired range of temperature is covered. From each set of isothermal data the complex plane plots are obtained and analyzed to check whether a semi-circular arc in accordance with Cole-Cole equation is obtained or whether a skewed arc in accordance with the Davidson-Cole equation is obtained.

The complex plane plots of polymers obtained by isothermal measurements do not lend themselves to the simple treatment that is used in case of simple molecules. The main reasons for this difficulty are: (1) The dispersion in polymers is generally very broad so that data from a fixed temperature are not sufficient for analysis of the dispersion. Data from several temperatures have to be pooled to describe dispersions meaningfully. (2) The shapes of the plots in the complex plane are rarely as simple as that obtained with

molecules of simpler structure rendering the determination of dispersion parameters very uncertain.

In an attempt to study the  $\alpha$ -dispersion in many polymers, Havriliak and Negami<sup>25</sup> have measured the dielectric properties of several polymers.  $\alpha$ -dispersion in a polymer is the process associated with the glass transition temperatures where many physical properties change in a significant way. In several polymers the complex plane plot is linear at high frequencies and a circular arc at low frequencies. Attempts to fit a circular arc (Cole-Cole) is successful at lower frequencies but not at higher frequencies. Likewise, an attempted fit with a skewed circular arc (Davidson-Cole) is successful at higher frequencies but not at lower frequencies.

The two dispersion equations, reproduced here for convenience, are represented by:

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = [1 + (j\omega\tau)^{1-\alpha}]^{-1} : \text{circular arc (Cole - Cole)}$$

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = (1 + j\omega\tau_0)^{-\beta} : \text{Skewed semicircle (Davidson - Cole)}$$

Combining the two equations, Havriliak and Negami proposed a function for the complex dielectric constant as

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = [1 + (j\omega\tau_{H-N})^{1-\alpha}]^{-\beta} \quad (3.72)$$

This function generates the previously discussed relaxations as special cases. When  $\beta = 1$  the circular arc shown above is generated. When  $\alpha = 0$  the skewed semicircle is obtained. When  $\alpha = 0$  and  $\beta = 1$  the Debye function is obtained. For convenience we omit the subscript H-N hereafter.

To test the relaxation function given by equation (3.72) we apply successively the DeMoivre's theorem and rationalize the denominator to obtain the expressions

$$\epsilon' - \epsilon_\infty = \frac{1}{r^{\beta/2}} (\epsilon_s - \epsilon_\infty) \cos(\beta\theta) \quad (3.73)$$

$$\varepsilon'' = \frac{1}{r^{\beta/2}} (\varepsilon_s - \varepsilon_\infty) \sin(\beta\theta) \quad (3.74)$$

where

$$r = [1 + (\omega\tau)^{1-\alpha} \sin(\frac{\alpha\pi}{2})]^2 + [(\omega\tau)^{1-\alpha} \cos(\frac{\alpha\pi}{2})]^2 \quad (3.75)$$

$$\theta = \arctan \left[ \frac{(\omega\tau)^{1-\alpha} \cos(\frac{\alpha\pi}{2})}{1 + (\omega\tau)^{1-\alpha} \sin(\frac{\alpha\pi}{2})} \right] \quad (3.76)$$

Equation (3.72) may be examined for extreme values of  $\omega$ , namely  $\omega \rightarrow \infty$  and  $\omega \rightarrow 0$ <sup>26</sup>.

For the first case, as  $\omega \rightarrow \infty$ , equation (3.72) becomes (for definition of  $\chi''$  see section 3.15)

$$\begin{aligned} \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} &\simeq (j\omega\tau)^{\beta(\alpha-1)} \\ &= (\omega\tau)^{\beta(\alpha-1)} \left\{ \cos[\beta(1-\alpha)\pi/2] - j \sin[\beta(1-\alpha)\pi/2] \right\}, \end{aligned}$$

$$\tan[\beta(1-\alpha)\pi/2] = \frac{\varepsilon''_{(\omega \rightarrow \infty)}}{\varepsilon'_{(\omega \rightarrow \infty)} - \varepsilon_\infty}$$

At very high frequencies  $\varepsilon'' \propto (\varepsilon' - \varepsilon_\infty) \propto \omega^{\beta(1-\alpha)}$

For the second case, as  $\omega \rightarrow 0$ ,

$$\begin{aligned} \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} &\simeq 1 - \beta(j\omega\tau)^{(1-\alpha)} \\ &= 1 - \beta(\omega\tau_H)^{(1-\alpha)} \left\{ \cos[(1-\alpha)\pi/2] + j \sin[(1-\alpha)\pi/2] \right\}, \end{aligned}$$

$$\tan\left(\frac{\alpha\pi}{2}\right) = \frac{\varepsilon''_{(\omega \rightarrow 0)}}{\varepsilon_s - \varepsilon'_{(\omega \rightarrow 0)}}$$

At very low frequencies,  $\varepsilon'' \propto (\varepsilon_s - \varepsilon') \propto \omega^{(1-\alpha)}$ . These results have led to the suggestion that the susceptibility functions have slopes as shown in the two extreme cases.

From equations (3.73) and (3.74) we note the following with regard to the dispersion parameter

I. As  $\omega\tau \rightarrow \infty$ ,  $\varepsilon' \rightarrow \varepsilon_\infty$  and  $\varepsilon'' \rightarrow 0$ . Therefore  $\varepsilon^* = \varepsilon_\infty$

II. As  $\omega\tau \rightarrow 0$ ,  $\varepsilon' \rightarrow \varepsilon_s$  and  $\varepsilon'' \rightarrow 0$ . Therefore  $\varepsilon^* \rightarrow \varepsilon_s$ .

We can therefore evaluate  $\varepsilon_s$  and  $\varepsilon_\infty$  from the intercept of the curve with the real axis. To find the parameters  $\alpha$  and  $\beta$  we note that equations (3.73) and (3.74) result in the expression

$$\frac{\varepsilon''}{\varepsilon' - \varepsilon_\infty} = \tan \beta\theta = \tan \phi \quad (3.77)$$

where we have made the substitution  $\beta\theta = \phi$ . By applying the condition  $\omega\tau \rightarrow \infty$  to equation (3.76) and denoting the corresponding value of  $\phi$  as  $\phi_L$  (see fig. 3.23) we get

$$\phi_L = (1 - \alpha)\beta\pi / 2 \quad (3.78)$$

which provides a relation between the graphical parameter  $\phi_L$  and the dispersion parameters,  $\alpha$  and  $\beta$ . Again the relaxation time is given by the definition  $\omega\tau \equiv 1$ , and let us denote all parameters at this frequency by the subscript p. Havriliak and Negami (1966) also prove that the bisector of angle  $\phi_L$  intersects the complex plane plot at  $\varepsilon_p^*$ . The point of intersection yields the value of  $\alpha$  by

$$\frac{1}{\phi_L} \log \frac{|\varepsilon_p^* - \varepsilon_\infty|}{\varepsilon_s - \varepsilon_\infty} = -\frac{1}{\pi(1 - \alpha)} \log[2 + 2 \sin \alpha(\pi / 2)] \quad (3.79)$$

The analysis of experimental data to evaluate the dispersion parameters is carried out by the following procedure from the complex plane plots:

1. The low frequency measurements are extrapolated to intersect the real axis from which  $\varepsilon_s$  is obtained.

2. The high frequency measurements are extrapolated to intersect the real axis from which  $\epsilon_\infty$  is obtained. If data on refractive index is available then the relation  $\epsilon_\infty = n^2$  may be employed in specific materials.
3. The parameter  $\phi_L$  is measured using the measurements at high frequencies.
4. The angle  $\phi_L$  is bisected and extended to intersect the measured curve. From the intersection point the frequency is determined and the corresponding relaxation time is calculated according to  $\omega = 1/\tau$ . The parameters  $\epsilon_p' - \epsilon_\infty$  and  $\epsilon''$  are also determined.
5. The parameter  $\alpha$  is decided by equation (3.79)
6. The parameter  $\beta$  is calculated by equation (3.78)

Havriliak and Negami analysed the data of several polymers and evaluated the five dispersion parameters ( $\epsilon_s$ ,  $\epsilon_\infty$ ,  $\alpha$ ,  $\beta$ ,  $\tau$ ) for each one of them (see chapter 5). A more recent list of tabulated values is given in Table 3.3<sup>27</sup>. The Havriliak and Negami function is found to be very useful to describe the relaxation in amorphous polymers which exhibit asymmetrical shape near the glass transition temperature,  $T_G$ . In the vicinity of  $T_G$  the  $\epsilon''$ - $\log\omega$  curves become broader as  $T$  is lowered. It has been suggested that the  $\alpha$ -parameter represents a quantity that denotes chain connectivity and  $\beta$  is related to the local density fluctuations. Chain connectivity in polymers should decrease as the temperature is lowered. The  $\alpha$ -parameter slowly increases above  $T_G$  which may be considered as indicative of this<sup>28</sup>. A detailed description of these aspects are treated in ch. 5.

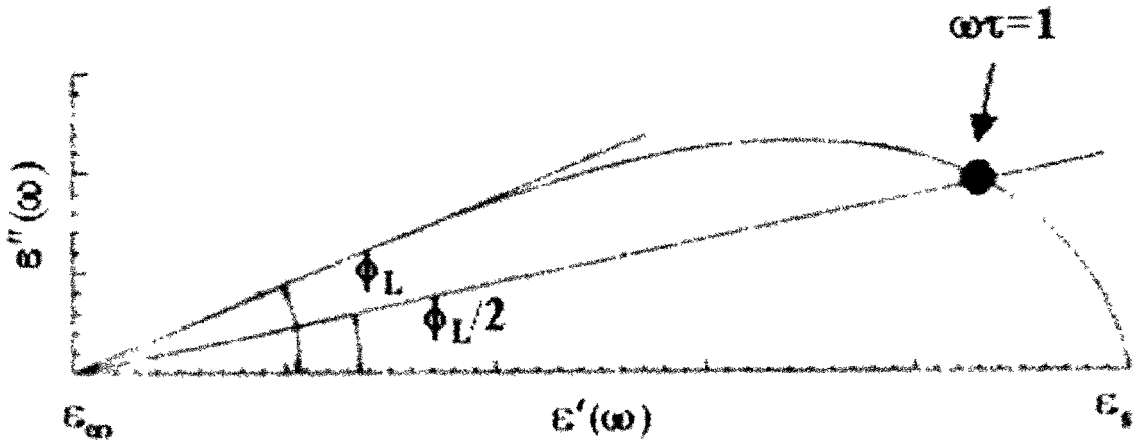


Fig. 3.23 Complex plane plot of  $\epsilon^*$  according to H-N function. At high frequencies the plot is linear. At low frequencies the plot is circular (Jonscher, 1999).

A final comment about the influence of conductivity on dielectric loss is appropriate here. As mentioned earlier measurement of  $\epsilon'' - \omega$  characteristics shows a sudden rise in the loss factor towards the lower frequencies, (e. g., see fig. 3.12) and this increase is due

to the dc conductivity of the material. The Havriliak-Negami function is then expressed as

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \left[ 1 + (j\omega\tau_0)^{(1-\alpha)} \right]^\beta - j \frac{\sigma_{dc}}{\omega \varepsilon_o}$$

where  $\sigma_{dc}$  is the dc conductivity.

### **3.15 DIELECTRIC SUSCEPTIBILITY**

In the published literature some authors<sup>29</sup> use the **dielectric susceptibility**,  $\chi^* = \chi' - j\chi''$  of the material instead of the dielectric constant  $\varepsilon^*$  and the following relationships hold between the dielectric susceptibility and dielectric constant:

$$\chi^* = \varepsilon^* - \varepsilon_\infty \quad (3.80)$$

$$\chi' = \varepsilon' - \varepsilon_\infty \quad (3.81)$$

$$\chi'' = \varepsilon'' \quad (3.82)$$

The last two quantities are often expressed as normalized quantities,

$$\chi' = \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty}; \chi'' = \frac{\varepsilon''}{\varepsilon_s - \varepsilon_\infty}$$

Equations (3.81) and (3.82) may also be expressed in a concise form as

$$\chi^* \propto \frac{1}{1 + j \frac{\omega}{\omega_p}}$$

where  $\omega_p$  is the peak at which  $\chi''$  is a maximum. Alternately we have

$$\chi^* \propto \frac{1}{1 + j\omega\tau} = \frac{1}{1 + \omega^2\tau^2} - \frac{j\omega\tau}{1 + \omega^2\tau^2} \quad (3.83)$$



Equation (3.83) is known as the **Debye Susceptibility function**. Expressing the dielectric properties in terms of the susceptibility function has the advantage that the slopes of the plots of  $\chi'$  and  $\chi''$  against  $\omega$  provide a convenient parameter for discussing the possible relaxation mechanisms. Fig. 3.24 (a) shows the variation of  $\chi'$  and  $\chi''$  as a function of frequency<sup>30</sup>. As discussed, in connection with the Debye equations, the decreasing part of  $\chi' \propto \omega^{-2}$ . The increasing part of  $\chi''$  at  $\omega \ll \omega_p$  changes in proportion to  $\omega^{+1}$  and the decreasing part of  $\chi''$  at  $\omega \gg \omega_p$  changes in proportion to  $\omega^{-1}$ .

**Table 3.4**

Selected Dispersion Parameters according to H-N Expression  
(Havriliak and Watts, 1986: with permission of Polymer)

| Polymer and Temperature              | $\epsilon_s$ | $\epsilon_\infty$ | $\log f_{\max}$ | $\alpha$ | $\beta$ |
|--------------------------------------|--------------|-------------------|-----------------|----------|---------|
| Poly(carbonate)                      | 3.64         | 3.12              | 6.85            | 0.77     | 0.29    |
| Polychloroprene (-26°C)              | 5.85         | 2.63              | 7.37            | 0.57     | 0.51    |
| Poly(cyclohexyl methacrylate) 121°C  | 4.33         | 2.45              | 5.33            | 0.71     | 0.33    |
| Poly(iso-butyl methacrylate) 102.8°C | 4.02         | 2.36              | 8.28            | 0.71     | 0.50    |
| Poly(n-butyl methacrylate) 59°C      | 4.29         | 2.44              | 7.06            | 0.62     | 0.60    |
| Poly(n-hexyl methacrylate) 48°C      | 3.96         | 2.48              | 4.40            | 0.74     | 0.66    |
| Poly(nonyl methacrylate) 42.8°C      | 3.51         | 2.44              | 8.18            | 0.73     | 0.65    |
| Poly(n-octyl methacrylate) 21.5°C    | 3.88         | 2.61              | 9.60            | 0.73     | 0.66    |
| Poly(vinyl acetal) 90°C              | 6.7          | 2.5               | 6.43            | 0.89     | 0.30    |
| Poly(vinyl acetate) 66°C             | 8.61         | 3.02              | 7.11            | 0.90     | 0.51    |
| Syndiotac-Poly(methyl methacrylate)  | 4.32         | 2.52              | 7.96            | 0.53     | 0.55    |
| Poly(vinyl formal)                   | 5.85         | 2.62              | 7.37            | 0.56     | 0.51    |

The Cole-Cole function has the form:

$$\chi^* \propto \frac{1}{1 + (j\omega\tau)^{1-\alpha}} \quad (3.84)$$

which is broader than the Debye function, though both are symmetrical about the frequency at which maximum loss occurs. The Davidson-Cole has the form

$$\chi^* \propto \frac{1}{[1 + (j\omega\tau)]^\beta} \quad (3.85)$$

These susceptibility functions are generalized and the relaxation mechanism is expressed in terms of two independent parameters,  $\alpha$  and  $\beta$ , by Havriliak and Negami, their susceptibility function having the form:

$$\chi^* = \frac{1}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \quad (3.86)$$

Figs. 3.24 (b) and (c) show the variation of these functions as a function of frequency. The similarities and divergences of these functions may be summarized as follows:

1. The Debye function is symmetrical about  $\omega_p$  and narrower than the Cole-Cole and Davidson-Cole functions. The low frequency region of the dispersion has a slope that is proportional to  $\omega$  and the high frequency region has a slope that is proportional to  $1/\omega$ . In this context the low frequency and high frequency regions are defined as  $\omega \ll \omega_p$  and  $\omega \gg \omega_p$ . In the high frequency region  $\chi'$  has a slope proportional to  $1/\omega^2$  (Fig. 3.24 a).
2. The Cole-Cole function (Fig. 3.24b) shows that  $\chi''$  has a slope proportional to  $\omega^{1-\alpha}$  in the low frequency region and a slope proportional to  $\omega^{\alpha-1}$  in the high frequency region. It is also symmetrical about  $\omega_p$ . The variation of  $\chi'$  in the high frequency region is also proportional to  $\omega^{\alpha-1}$ .
3. The Davidson-Cole susceptibility function (Fig. 3.24 c) is asymmetrical about the vertical line drawn at  $\omega_p$ . In the low frequency region  $\chi''$  is proportional to  $\omega$  which is a behavior similar to that of Debye. In the high frequency region  $\chi''$  is proportional to  $\omega^{-\beta}$ . The real part of the susceptibility function,  $\chi'$ , in the high frequency region is also proportional to  $\omega^{-\beta}$ . It should be borne in mind that the Cole-Cole and Davidson -Cole susceptibility functions have a single parameter, whereas the Debye function has none.

To demonstrate the applicability of Davidson-Cole function we refer to the measurement of dielectric properties of glycerol by Blochowicz et. al. (1999) over a temperature range of 75-296 K and a frequency range of  $10^{-2} \leq f \leq 3000$  MHz. A plot  $\epsilon''(f)$  as a function of  $\log(f)$  is shown in fig. 3.16. At  $f < f_{\max}$ ,  $\epsilon''$  behaves similar to a Debye function but at  $f > f_{\max}$ , there are two slopes,  $-\beta$  and  $-\gamma$  appearing in that order for increasing frequency.

Since Davidson-Cole function uses one parameter only a modification to equation (3.85) is proposed by Blochowicz et. al (1999).

$$\chi^* = \frac{\left(1 + \frac{j\omega_o\tau_o}{C_o}\right)^{\beta-\gamma}}{(1 + j\omega\tau_o)^\beta}$$

Here  $\tau_o = 1/\omega_p$  and  $C_o$  is a parameter that controls the frequency of transition from  $\beta$ -power law to  $\gamma$ -power law.

The condition  $\beta = \gamma$  signifying a single slope for the  $\log f$ - $\epsilon''$  yields Davidson-Cole function because the two slopes merge into one. The mean relaxation time is obtained by the relation

$$\tau = \lim_{\omega \rightarrow 0} \frac{\epsilon''}{\omega} = \beta\tau_o - (\beta - \gamma) \frac{\tau_o}{C_o} = \beta\tau_o$$

The temperature dependence of  $\beta$ ,  $\gamma$  and  $C_o$  is shown in their fig. 4(b).  $\beta$  is weakly dependent on  $T$  whereas  $\gamma$  increases rapidly to approach  $\beta$ .

At the glass transition temperature the two power laws merge into one in accordance with equation (3.85). The relaxation in the glass phase ( $T < T_g$ ) is determined by a single power law over a wide frequency range of  $10^{-2} < f < 10^5$  Hz. Below  $T_g$  the co-efficient  $\gamma$  is not temperature dependent and very similar for many systems exhibiting this type of behavior. For glycerol  $\gamma = 0.07 \pm 0.02$ . The behavior below  $T \ll T_g$  occurs according to  $\chi'' = \omega^\gamma$ . The high frequency contribution of  $\alpha$ -relaxation is frozen out at  $T \ll T_g$ . If the data on  $\chi''$  is replotted in the  $T$  domain at  $f = 1$  Hz an exponential relationship is obtained according to

$$\chi'' = e^{T/T_f}$$

where  $T_f$  is a constant that is dependent on the material. Their fig. (6a) shows this relationship for many substances, the departure from this equation being due to the onset of the  $\alpha$ -process.

4. The Havriliak-Negami function is more general because of the fact that it has two parameters. The comments made with regard to equations(3.73) and (3.74) are equally

applicable to their susceptibility functions; we get the three functions listed above as special cases:

- (i)  $\alpha = 0$  and  $\beta=1$  gives the Debye equation
- (ii)  $0 < \alpha < 1$  and  $\beta=1$  gives the Cole-Cole function
- (iii)  $\alpha = 0$  and  $0 < \beta < 1$  gives the Davidson-Cole function

Though this susceptibility function has two parameters which are independently adjustable, the low frequency behavior is not entirely independent of the high frequency behavior. This is due to the fact that the parameter  $\alpha$  appears in both the expressions for  $\chi'$  and  $\chi''$ .

The parameters  $\alpha$  and  $\beta$  have no physical meaning though these models are successful in fitting the measured data to one of these functions. It has been suggested that a distribution of relaxation times is usually associated with one of the Cole-Cole, Davidson-Cole, and Havriliak-Negami functions. In these models the observed dielectric response is considered as a summation, through a distribution function  $G(\tau)$ , of individual Debye responses for each group.

### **3.16 DISTRIBUTION OF RELAXATION TIMES**

We have already considered the situations in which there are more than a single relaxation time (section 3.6) and we intend to examine this topic more closely in this section. Polymers generally have a number of relaxation times due to the fact that the long chains may be twisted in a complex array of molecular segments or due to the complicated energy distribution in crystalline regions of the polymer. Since the distribution function is denoted by  $G(\tau)$  the fraction of dipoles having relaxation times between  $\tau$  and  $\tau + \Delta\tau$  is given as  $G(\tau) d\tau$  and hence for all dipoles

$$\int_0^{\infty} G(\tau) d\tau = 1 \quad (3.87)$$

Assuming that each differential group of dipoles with different relaxation times follows Debye behavior non-interactively, the complex dielectric constant becomes:

$$\epsilon^* = \epsilon_{\infty} + (\epsilon_s - \epsilon_{\infty}) \int_0^{\infty} \frac{G(\tau) d\tau}{1 + j\omega\tau} \quad (3.88)$$

By separating the real and imaginary parts of equations (3.88), the dielectric constant and the loss factor are expressed as

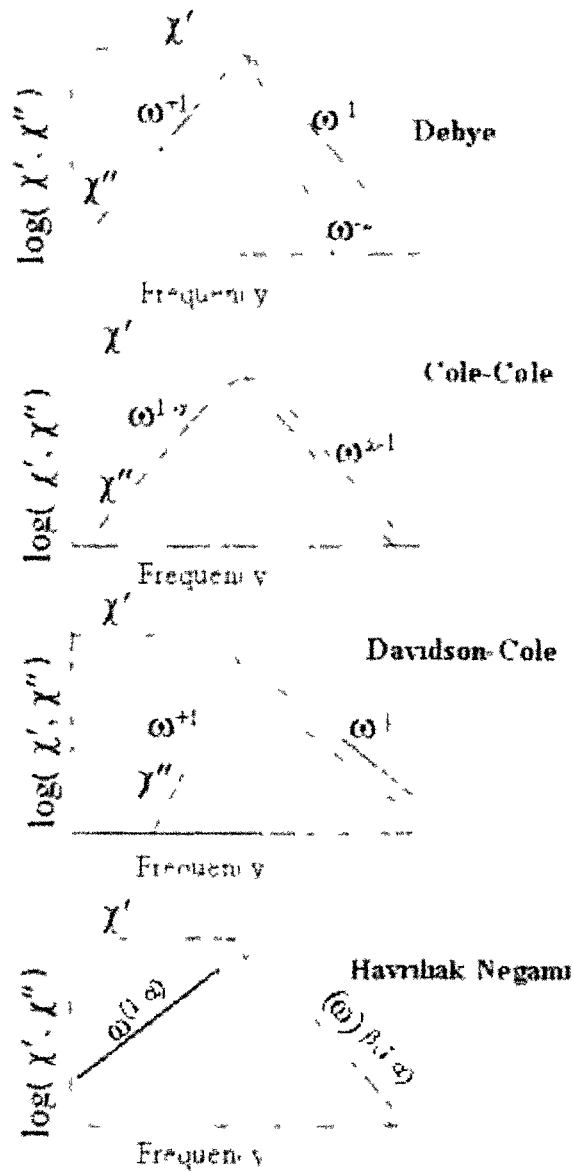


Fig. 3.24 Frequency dependence of susceptibility functions (Das Gupta and Scarpa, ©1999, IEEE). H-N relaxation has been added by the author.

$$\varepsilon' = \varepsilon_{\infty} + (\varepsilon_s - \varepsilon_{\infty}) \int_0^{\infty} \frac{G(\tau) d\tau}{1 + \omega^2 \tau^2} \quad (3.89)$$

$$\varepsilon'' = (\varepsilon_s - \varepsilon_{\infty}) \int_0^{\infty} \frac{\omega \tau G(\tau) d\tau}{1 + \omega^2 \tau^2} \quad (3.90)$$

The susceptibility function is expressed as:

$$\chi^* = \int_0^{\infty} \frac{G(\omega)}{1 + j\omega\tau} d\tau \quad (3.91)$$

In some texts (Vera Daniel, 1967) the normalization of equation (3.87) is carried out by expressing the right hand side of equation (3.87) as  $(\varepsilon_s - \varepsilon_{\infty})$ . This results in the absence of this factor in the last term in equations (3.88) - (3.90). The existence of a distributed relaxation time explains the departure from the ideal Debye behavior in the susceptibility functions. However it has been suggested that a distribution of relaxation times cannot be correlated with the existence of relaxing entities in a solid, to justify physical reality.

Equations (3.89) and (3.90) are the basis for determining  $G(\tau)$  from  $\varepsilon'$  and  $\varepsilon''$  data though the procedure, as mentioned earlier, is not straight forward. Simple functions of  $G(\tau)$  such as Gaussian distribution lead to complicated functions of  $\varepsilon'$  and  $\varepsilon''$ . On the other hand, simple functions of  $\varepsilon'$  and  $\varepsilon''$  also lead to complicated functions of  $G(\tau)$ .

Fig. 3.25 helps to visualize the continuous distribution of relaxation times according to H-N expression for various values of the parameter  $\beta$  and  $\alpha\beta=1$  using expressions to follow<sup>31</sup>. The corresponding complex plane plots are also shown.

It is helpful to express equations (3.89) and (3.90) as (Williams, 1963)

$$J_{\omega} = \frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_s - \varepsilon_{\infty}} = \int_0^{\infty} \frac{G(\tau)}{1 + \omega^2 \tau^2} \quad (3.92)$$

$$H_{\omega} = \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_{\infty}} = \int_0^{\infty} \frac{G(\tau) \omega \tau}{1 + \omega^2 \tau^2} d\tau \quad (3.93)$$

To demonstrate the usefulness of equations (3.92) and (3.93) the measured loss factor in amorphous polyacetaldehyde (Williams, 1963) over a temperature range of  $-9^{\circ}\text{C}$  to  $+34.8^{\circ}\text{C}$  and a frequency range of 25Hz-100kHz is shown in Fig. 3.26. Polyacetaldehyde is a polar polymer with its dielectric moment in the main chain, similar to PVC. Its monomer has a molecular weight of 44 and it belongs to the class of atactic polymers. Its refractive index is 1.437. A single broad peak was observed at all temperatures.

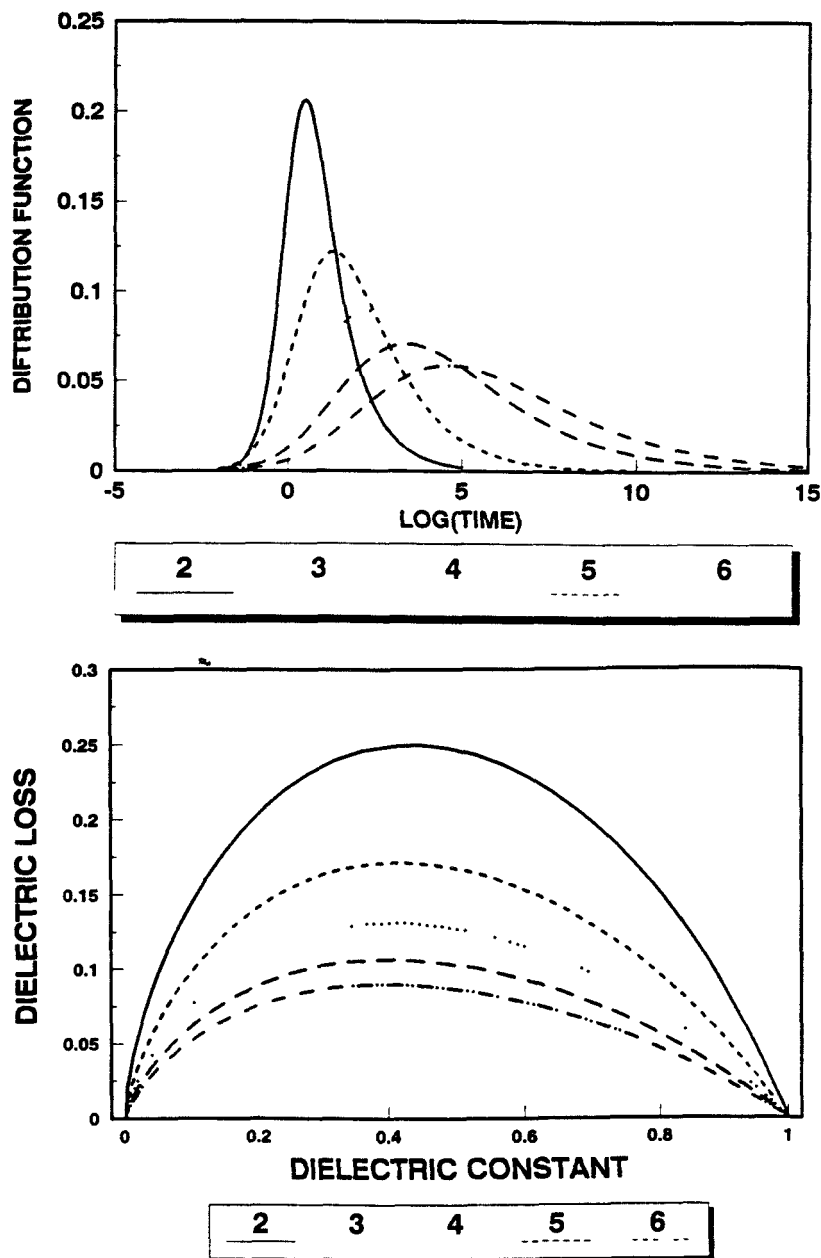


Fig. 3.25 Distribution of relaxation times for various values of  $\beta$  according to H-N dispersion. The corresponding complex plane plots of  $\epsilon^*$  are also shown for  $\alpha\beta=1$  [Runt and Fitzgerald, 1997]. (with permission of Am. Chem. Soc.).

Fig. 3.27 shows these data replotted as  $J_\omega$  and  $H_\omega/H_{\omega p}$  as a function of  $(\omega/\omega_p)$ . The experimental points all lie on a master curve indicating that the shape of the distribution of relaxation times is independent of the temperature.

Evaluation of the distribution function from such data is a formidable task requiring a detailed knowledge of Laplace transforms. The relaxation time distribution appropriate to the Cole-Cole equation is<sup>32</sup>

$$G(\tau) = \frac{\sin \alpha \pi}{2\pi \cosh[(1 - \alpha) \ln \tau / \tau_0] - \cos \alpha \pi} \quad (3.94)$$

in which  $\tau_0$  is the relaxation time at the center of the distribution.

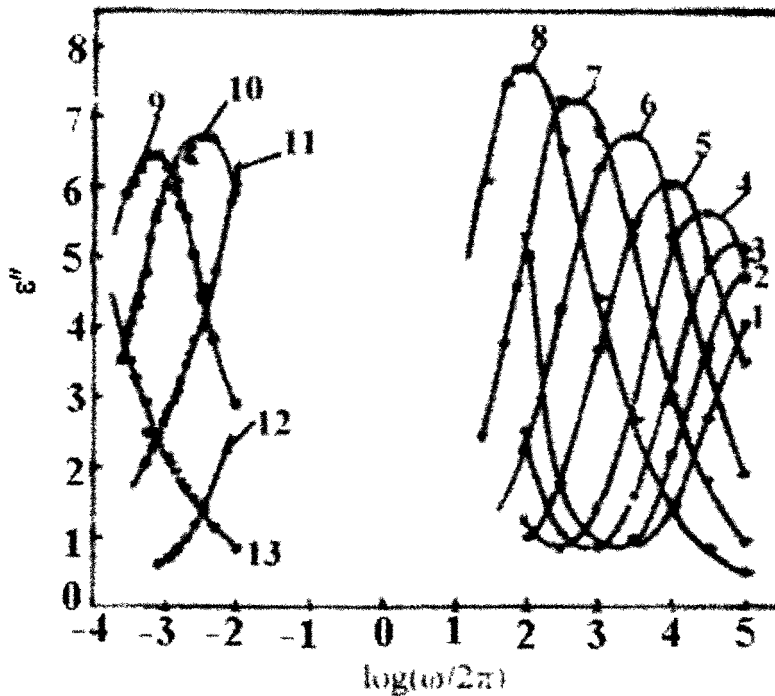


Fig. 3.26 Plot of  $\epsilon''$  against  $\log(\omega/2\pi)$  for 0.598 thick sample. 1-34.8°C, 2-30.5 °C, 3-25 °C, 4-18.5 °C, 5-9.7 °C, 6-3.25 °C, 7-3.5 °C, 8--9 °C, 9-19.2 °C, 10-21.8 °C, 11-24.5 °C, 12-26.4 °C, 13-28.7 °C [Williams, 1963] (with permission of Trans. Farad. Soc.).

As demonstrated earlier (fig. 3-10) the complex plane plot of the Cole-Cole distribution is symmetrical about the mid point and therefore the plot of  $G(\tau)$  against  $\log \tau$  or  $\log(\tau/\tau_{\text{mean}})$  will be symmetrical about the line. The graphical technique for the analysis of dielectric data makes use of fig. 3.9. The quantity  $u/v$  is plotted against  $\log v$  and the



result will be a straight line of slope  $1-\alpha$ . Without this verification the Cole-Cole relationship cannot be established with certainty.

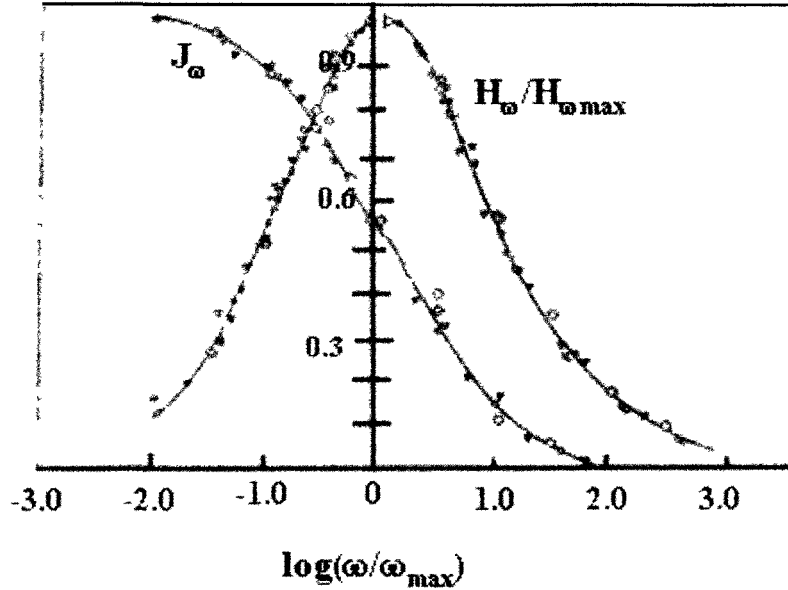


Fig. 3.27 Master curves for  $J_\omega$ , eq. (3.92) and  $H_\omega/H_{\omega_{\max}}$ , eq. (3.93) as a function of  $\log(\omega/\omega_{\max})$ . 0.598 thick sample. Symbols are the same as in fig. 3-26 [Williams, 1963]. Adopted with permission of Trans. Farad. Soc.]

The distribution of relaxation time according to Davidson-Cole function is

$$G(\tau) = \frac{\sin \beta \pi}{\pi} \left( \frac{\tau}{\tau_0 - \tau} \right)^\beta \quad \tau < \tau_0 \quad (3.95)$$

$$= 0 \quad \tau > \tau_0 \quad (3.96)$$

The distribution of relaxation times for the Fuoss-Kirkwood function is a logarithmic function:

$$G(\tau) = \frac{\partial}{\partial} \frac{\cos(\frac{\partial \pi}{2}) \cosh(\partial s)}{\pi \cos^2(\frac{\partial \pi}{2}) + \sinh^2(\partial s)} \quad (3.97)$$

Where  $\delta$  is a constant defined in section (3.12) and  $s = \log(\omega/\omega_p)$ . The distribution of relaxation times for H-N function is given by [Havriliak and Havriliak, 1997]

$$G(\tau) = \left(\frac{1}{\pi}\right) y^{\alpha\beta} (\sin \beta\theta) (y^{2\alpha} + 2y^\alpha \cos \pi\alpha + 1)^{-\beta/2} \quad (3.98)$$

In this expression

$$y = \frac{\tau}{\tau_0} \quad (3.99)$$

$$\theta = \arctan\left(\frac{\sin \pi\alpha}{y^\alpha + \cos \pi\alpha}\right) \quad (3.100)$$

The distribution of relaxation times may also be represented according to an equation of the form, called Gaussian function (Hasted, 1973) given by

$$G(\tau) = \left(\frac{1}{\sigma\sqrt{2\pi}}\right) \exp\left\{\left(-\frac{1}{2}\right)\left(\frac{y}{\sigma}\right)^2\right\} \quad (3.101)$$

where  $\sigma$  is known as the standard deviation and indicates the breadth of the dispersion. From the form of this function it can be recognized that the distribution, and hence the  $\epsilon''$ - $\omega$  plot, will be symmetrical about the central or relaxation time (fig. 3.28). As the standard deviation increases the  $\log(\epsilon'') - \log(\omega)$  plots become narrower, and for the case  $1/\sigma = 0$ , the distribution reduces to a single relaxation time of Debye relaxation. In fig. 3.28 the frequency is shown as the variable on the x-axis instead of the traditional  $\tau/\tau_{\text{mean}}$ ; conversion to the latter variable is easy because of the relationship  $\omega\tau=1$ . In almost every case the actual distribution is difficult to determine from the dielectric data whereas its width and symmetry are easier to recognize.

A simple relationship between  $(\epsilon_s - \epsilon_\infty)$  and  $\epsilon''$  may be derived<sup>33</sup>. The area under the  $\epsilon''$ - $\log \omega$  curve is

$$\int_0^\infty \epsilon'' d(\ln \omega) = (\epsilon_s - \epsilon_\infty) \int_{\tau=0}^\infty \int_{\omega=0}^\infty \frac{G(\tau)\omega\tau}{1 + \omega^2\tau^2} d\tau d(\ln \omega) \quad (3.102)$$

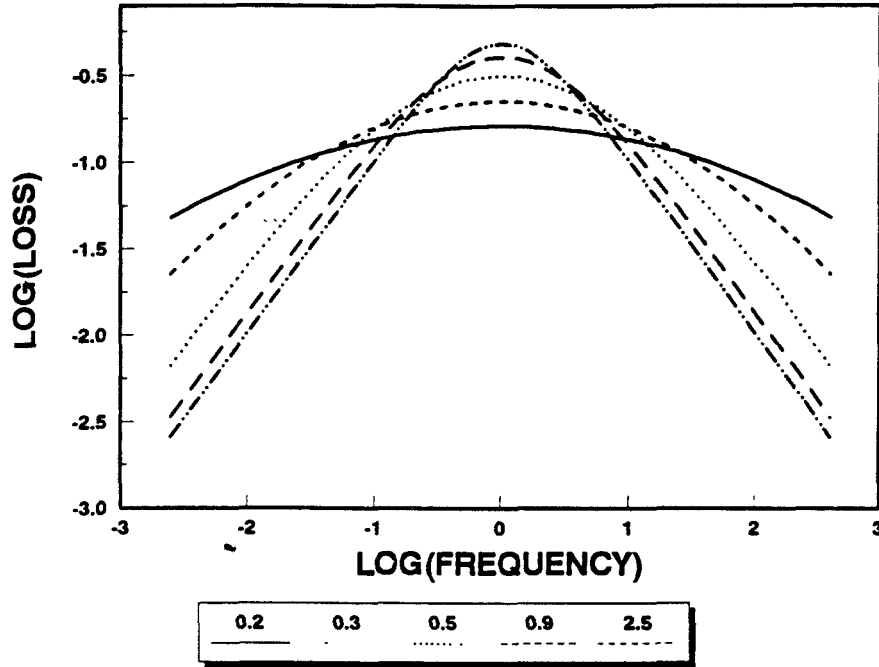


Fig. 3.28 Log  $\epsilon''$  against log(frequency) for Gaussian distribution of relaxation times. The numbers show the standard deviation,  $\sigma$ . Debye relaxation is obtained for  $1/s=0$ . Note that the slope at high frequency and low frequency tends to +1 and -1 as  $\sigma$  increases.[Havriliak and Havriliak, 1997]. (Permission of Amer. Chem. Soc.)

Using the identity

$$\int_0^{\infty} \frac{\omega \tau}{1 - \omega^2 \tau^2} d(\ln \omega) = \frac{\pi}{2}$$

expression (3.102) simplifies into, because of equation (3.87),

$$\int_0^{\infty} \epsilon'' d(\ln \omega) = \int \frac{\epsilon'' d\omega}{\omega} = \frac{\pi}{2} (\epsilon_s - \epsilon_{\infty}) \quad (3.103)$$

The inversion formula corresponding to equation (3.103) is

$$\epsilon'' \cong -\frac{\pi}{2} \frac{\partial \epsilon'}{\partial (\ln \omega)} \quad (3.104)$$

which is useful to calculate  $\epsilon''$  approximately.

Equation (3.103) may be verified in materials that have Debye relaxation or materials that have a peak in the  $\epsilon'' - \log \omega$  characteristic though the peak may be broader than that for Debye relaxation. Such calculations have been employed by Reddish<sup>34</sup> to obtain the dielectric constant of PVC and chlorinated PVC (see Chapter 5). For measurements the frequency range can be extended by making measurements at different temperatures because  $\omega_p$ ,  $\tau$  and  $T$  are related through equations

$$\omega_p \tau = 1 \quad (3.105)$$

$$\tau = \tau_0 \exp \frac{w}{kT} \quad (3.106)$$

Fig. 3.29 (Hasted, 1963) summarizes the dielectric properties  $\epsilon' - \epsilon''$  in the complex plane, the shape of the distribution of relaxation time and the decay function which will be discussed in chapter 6.

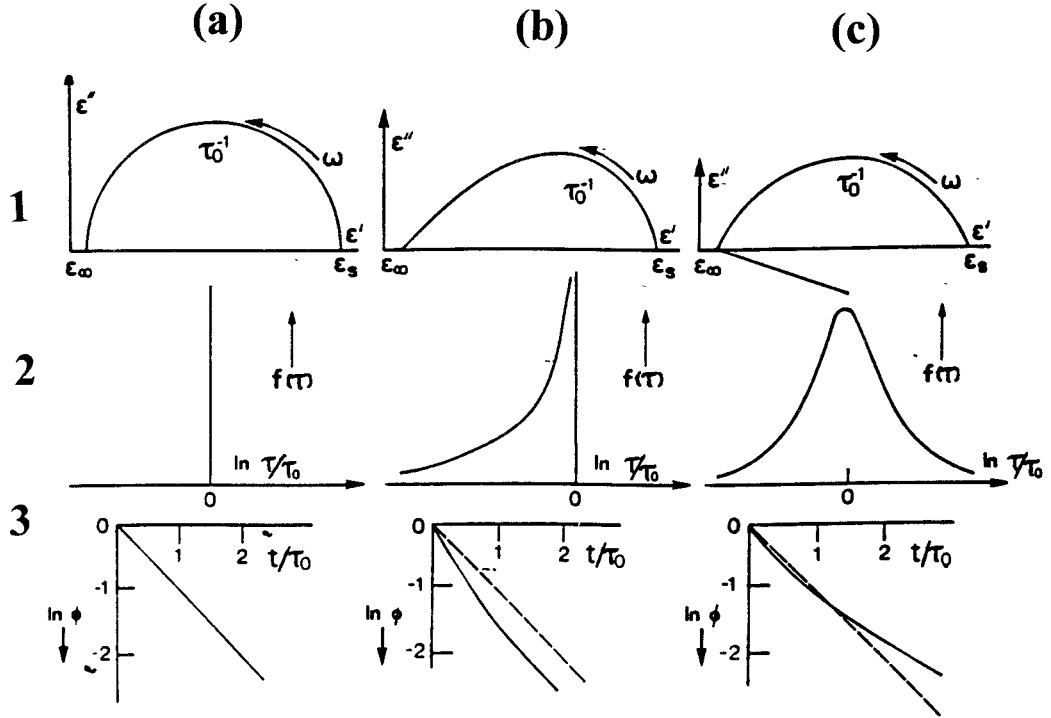
### **3.17 KRAMER-KRONIG RELATIONS**

Expressions (3.89) and (3.90) use the same relaxation function  $G(\tau)$  and in principle we must be able to calculate one function if the other function is known. This is true only if  $\epsilon'$  are related  $\epsilon''$  and these relations are known as Kramer-Konig relations<sup>35</sup>:

$$\epsilon'(\omega) - \epsilon_\infty = \frac{2}{\pi} \int_0^\infty \frac{x \epsilon''(x)}{x^2 - \omega^2} dx \quad (3.107)$$

$$\epsilon''(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{\epsilon' - \epsilon_\infty}{x^2 - \omega^2} dx \quad (3.108)$$

Integration is carried out using an auxiliary variable  $x$  which is real. Equations (3.107) and (3.108) imply that at  $\omega = \infty$ ,  $\epsilon' = \epsilon_\infty$  and  $\epsilon'' = 0$ . Daniel (1967) lists the conditions to be satisfied by a system so that these equation are generally applicable. These are:



Time Variation of polarization

Fig. 3.29 Graphical depiction of dielectric parameters for the three relaxations shown at top. The applicable equations are also shown (Hasted, 1973). (with permission of Chapman and Hall). Row and column designations are: a1 = eq. (3.31), b1 = eq. (3.53), c1 = eq. (3.45), a2 = single value, eq. (3.31), b2 = eq. (3.95), c2 = eq. (3.94), See chapter 6 for row 3, a3 = eq. (6.46), b3 = eq. (6.49), c3 = eq. (6.47) and (6.48).

1. The system is linear.
2. The constitution of the system does not change during the time interval under consideration.
3. The response of the system is always attributed to a stimulus.

There is no advantage in deriving these equations as we are mostly interested in their application. Application of Kramer-Kronig relations is laborious if the known values are not analytical functions of  $\omega$ . Jonscher<sup>36</sup> lists a computer program for numerical computation. However the area of the curve  $\epsilon'' - \ln \omega$  readily gives  $(\epsilon_s - \epsilon_\infty)$  according to the equation (3.103). Kramer-Konig relations have been used to derive  $\epsilon'$  from  $\epsilon'' - \omega$

data and compared with measured  $\epsilon'$  as a means of verifying assumed  $\epsilon'' - \omega$  relationship<sup>37</sup>.

### **3.18 LOSS FACTOR AND CONDUCTIVITY**

Many dielectrics possess a conductivity due to motion of charges and such conductivity is usually expressed by a volume conductivity. The motion of charges in the dielectric gives rise to the conduction current and additionally polarizes the dielectric. The conductivity may therefore be visualized as contributing to the dielectric loss. Equation (3.8) gives the contribution of conductivity to the dielectric loss. The loss factor is expressed as

$$\epsilon'' = \epsilon''(\omega) + \frac{\sigma}{\omega \epsilon_0} \quad (3.109)$$

Substituting, for  $\epsilon''(\omega)$ , from equation (3.29) one gets

$$\sigma = (\epsilon_s - \epsilon_\infty) \epsilon_0 \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \quad (3.110)$$

If one substitutes

$$\sigma_\infty = \frac{(\epsilon_s - \epsilon_\infty) \epsilon_0}{\tau} \quad (3.111)$$

one obtains

$$\sigma = \frac{\sigma_\infty \omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (3.112)$$

The conductivity increases from zero at  $\omega = 0$  to infinity at  $\omega = \infty$  in a manner similar to the mirror image of the decrease of  $\epsilon'$  with increasing  $\omega$  (fig. 3.3). If d.c. conductivity exists then the total conductivity is given by

$$\sigma_{\text{Total}} = \sigma_{\text{dc}} + \frac{(\sigma_\infty - \sigma_{\text{dc}}) \omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (3.113)$$

Jonscher has compiled the conductivity as a function of frequency in a large number of materials<sup>38</sup> and suggested a “Universal” power law according to

$$\sigma(\omega) = \sigma_{\text{dc}} + a\omega^n \quad (3.114)$$

where the exponent is observed to be within  $0.6 \leq n \leq 1$  for most materials. The exponent either remains constant or decreases slightly with increasing temperature and the range mentioned is believed to suggest hopping of charge carriers between traps. The real part of the dielectric constant also increases due to conductivity. A relatively small increase in  $\epsilon'$  at low frequencies or high temperatures is possibly due to the hopping charge carriers and a much larger increase is attributed to the interfacial polarization due to space charge, as described in chapter 4.

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